www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Arch. Metall. Mater. **63** (2018), 2, 1055-1059

DOI: 10.24425/122442

TAE GYU PARK*, SANG HYUN LEE**, BIN LEE**, HYE MI CHO**,
WON JUNG CHOI**, BUM SUNG KIM**, KWANG SEON SHIN*#, TAEK-SOO KIM*#

FABRICATION AND CHARACTERIZATION OF CoCrFeNiMn HIGH ENTROPY ALLOY POWDER PROCESSED BY GAS ATOMIZATION

In this study, precisely controlled large scale gas atomization process was applied to produce spherical and uniform shaped high entropy alloy powder. The gas atomization process was carried out to fabricate CoCrFeNiMn alloy, which was studied for high ductility and mechanical properties at low temperatures. It was confirmed that the mass scale, single phase, equiatomic, and high purity spherical high entropy alloy powder was produced by gas atomization process.

The powder was sintered by spark plasma sintering process with various sintering conditions, and mechanical properties were characterized. Through this research, we have developed a mass production process of high quality and spherical high entropy alloy powder, and it is expected to expand applications of this high entropy alloy into fields such as powder injection molding and 3D printing for complex shaped components.

Keywords: High entropy alloy, Gas atomization, Spark plasma sintering, CoCrFeNiMn

1. Introduction

The design and development of new alloys having superior mechanical properties (high strength, hardness, ductility, and mechanical properties at high/low temperatures) is getting spotlight due to advances in extreme environment applications in fields like aerospace, national defense, and cryogenic processing industries.

High entropy alloy (HEA), which for the first time was developed and defined by Prof. Yeh in 2004, was a turning point in the paradigm of conventional alloys [1-5]. HEA is an alloy, in which 5 or more elements are added in a similar ratio; not having a base material which occupies a high content. Studies on the composition, production method and properties of the HEAs have been continuously reported, CoCrFeNiMn composition has shown noticeable performance [6]. It exhibits a remarkably high ductility, and maintains its performance even at very low temperatures, thus showing the possibility of applications to various purposed structural materials.

In the case of cryogenic materials, there is a wide variety of applications, such as barriers and pipes for ships and offshore structures, as well as small, high-precision parts such as valves, pistons, and packings. Generally, a powder metallurgy process is applied to manufacture high quality, small-sized, high-precision parts. There are several researches on the production of HEA powder by mechanical alloying. Mechanical alloying processes, such as high energy milling process can synthesis precise controlled alloy composition, However, these processes are not suitable for mass production of the powders, and the shape of the powder produced is not uniform [7]. In order to form precise shape through metal injection molding process or 3D printing process, it is necessary to manufacture spherical uniform powder.

Recent researches on the preparation of HEA powder using gas atomization have been reported [8]. They succeeded in producing well-alloyed HEA powder, and proceeded with sintering, and confirmed the possibility of expanding the applications of the HEA powders. However, previous researches were focused on the production of small amounts of high quality powder. In order to introduce the superior characteristics of the HEAs into the commercial stage, it is essential to develop a mass production process.

In this study, we aim to develop a mass production technology of HEA powder using a large capacity (20 kg) atomizer. Since the heat capacity is large, and the volatilization control of the alloy melt and the gas injection related parameters are important compared to the powder production using a small atomizer, the crucible selection, temperature increase rate, and gas injection pressure were precisely controlled. Sintering was carried out by SPS (Spark Plasma Sintering) in order to observe the sinterability of the prepared HEA powders.

* SEOUL NATIONAL UNIVERSITY, SEOUL, REPUBLIC OF KOREA
** KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY, INCHEON, REPUBLIC OF KOREA
# Corresponding authors: ksshin@snu.ac.kr, tskim@kitech.re.kr

2. Experimental

In this study, a high capacity gas atomizer (Dongyang Induction Melting Furnace, Republic of Korea) using Ar gas was used for the production of high purity spherical HEA powder. Co (99.99%, all powders were served by Hana alloy, Republic of Korea), Cr (99.5%), Fe (99.9%), Ni (99.9%), and Mn (99.5%) were used as the raw materials, and the mother alloy was first prepared by using a vacuum induction melting furnace. The prepared mother alloy was heated up to about 1700°C in an argon atmosphere using a vacuum induction melting furnace, and a magnesia crucible was used. The molten metal, which leaked through a 4.5 mm diameter orifice, was sprayed with 25 bar of Ar gas to form spherical CoCrFeNiMn HEA powder. The fabricated powder particles were automatically separated by particle size.

The microstructure of the powders were observed using SEM (Scanning electron microscopy, JEOL Ltd., JSM-7100F) and EDS (Energy-dispersive Spectrometer, JEOL). XRD (X-ray diffraction, Bruker Inc., D8 Advance) analysis was performed to confirm the crystallization of the synthesized powders. To investigate the changes of powder characteristics with particle size and cooling rate, large sized powder (100~150 μm) and small powder (<53 μm) were selected and characterized.

Small sized powder (<53 μm) was filled in graphite mold and sintering of the HEA powder was performed by SPS (Weltech, Republic of Korea). Vacuum condition of the sintering process was $5.0*10^{-3}$ torr, and a pressure of 45 MPa was applied. In order to optimize the sintering temperature, the powder was heated to 700, 800, 900, 1000°C separately, and maintained for 2, 4, 6, 8 and 10 min respectirely. The sintered samples were analyzed by EBSD (Electron backscatter diffraction, JEOL, Japan) analysis to observe the change of microstructure according to sintering conditions. Mechanical property of the sintered body was measured by the Vickers indentation method (Mitutoyo, Japan). The measurements were conducted for each sintered body for at least 10 time under a load of 9.8 N with a loading time of 10 seconds.

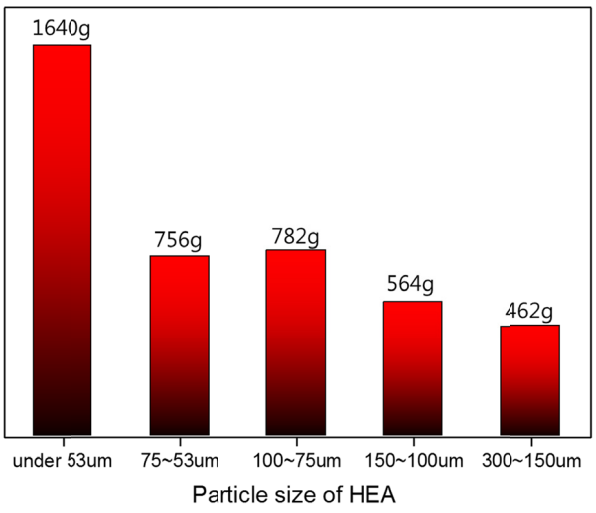

Fig. 1. Powder size distribution of gas atomized CoCrFeNiMn HEA powder

3. Results and discussion

A 20 kg scale gas atomizer was used for the preparation of the CoCrFeNiMn HEA powder. The total amount of alloy was adjusted to 10 kg, and each component was charged with the same mole fraction. The most important meaning of this study is the mass production of the high-quality spherical HEA powder. Through the precise optimization of manufacturing process, we succeeded in manufacturing 4.2 kg spherical powder using 10 kg raw materials. The particle size distribution of the spherical powder is shown in figure 1.

The microstructures of the large powder (100~150 μm) and the small powder (<53 μm) were analyzed, as shown in figure 2. Although the large sized powders have some irregular shape and contain small satellites on the surface of powders (Fig. 2(a)), overall, the powders larger than 150 um showed spherical shape. Small

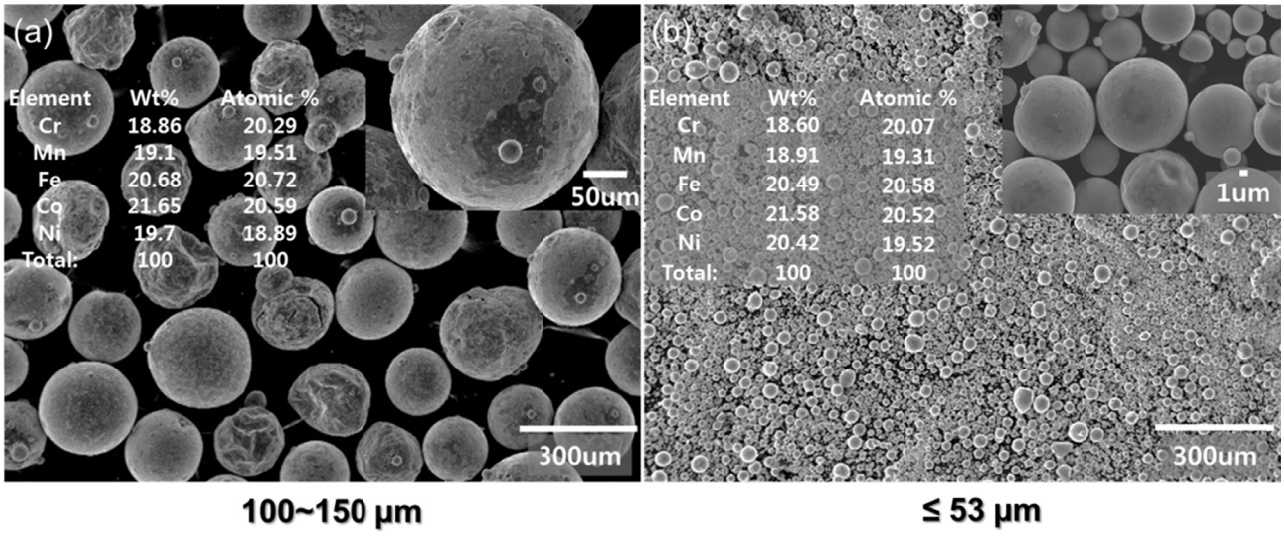

Fig. 2. Microstructure and surface elemental analysis of atomized HEA powder (a) 100~150 μm large sized powders, (b) <53 μm small sized powder

powders which have under 53 um have almost perfect spherical shape and smooth surface without satellites or defects (Fig. 2(b)).

In order to confirm the formation of homogeneous HEA powder by gas atomization process, XRD and EDS analysesof atomized powders were conducted (Fig. 3). Before the atomization process, there was pre-alloying process for Co, Cr, Fe, Ni, and Mn elemental lumps via induction melting process. However, if the atomization process were not precisely controlled, each element would separate from one another or form dendrite structures during re-melting and cooling steps. First, XRD was analyzed to see if the five elements form a single phase without being separated. XRD pattern of atomized powder clearly showed simple and clear FCC phase (Fig. 3(a)). Following EDS results of the cross-section of the powder confirmed that the five elements were almost uniformly mixed. Those tendencies were confirmed in both large and small sized powders (Fig. 3(b)).

Microstructural changes of powders during rapid cooling process were analyzed by EBSD of powders (Fig. 4). It could be assumed that the cooling speeds of the small and large sized powders were different, and they would show different grain size and shape. Importantly, the dendrite structures, which were commonly observed in the atomized HEA powders inother studies, were not found in this study. The secondary phase formation was suppressed by the optimized crucible with the minimum contamination, and the rapid gas atomization process resulted in rapid cooling of the powders. Even the big sized powders (100~150 μm, Fig. 4(b)) do not contain any dendrite structures or second phase.

SPS process was conducted to confirm of the formability and mechanical property of spherical powder HEA which was processed by gas atomizing process. Small sized powder (<53 μm) was used for SPS process. In order to optimize the sintering temperature, XRD, sintering density and hardness were measured by varying the temperature from 700°C to 1000°C by 100°C for 2 minutes increment each. From the relative density and hardness results, 900°C was found as could be optimized sintering temperature for the spherical shaped CoCrFeNiMn HEA powder.

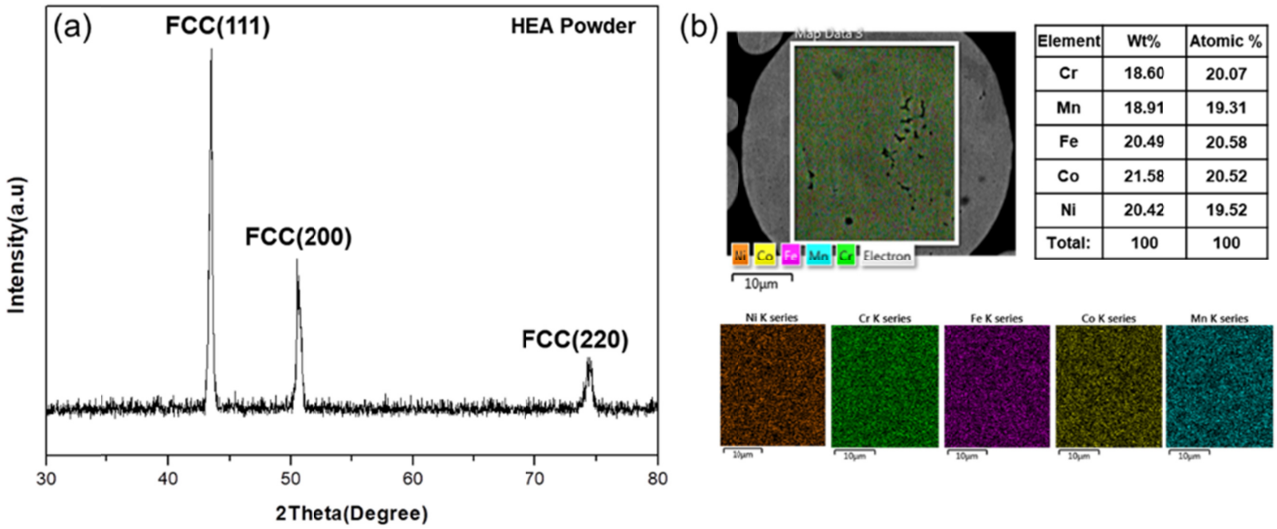

Fig. 3. Structural and elemental analysis of atomized HEA powder (a) XRD analysis of the powder, (b) polished inner surface of the powder

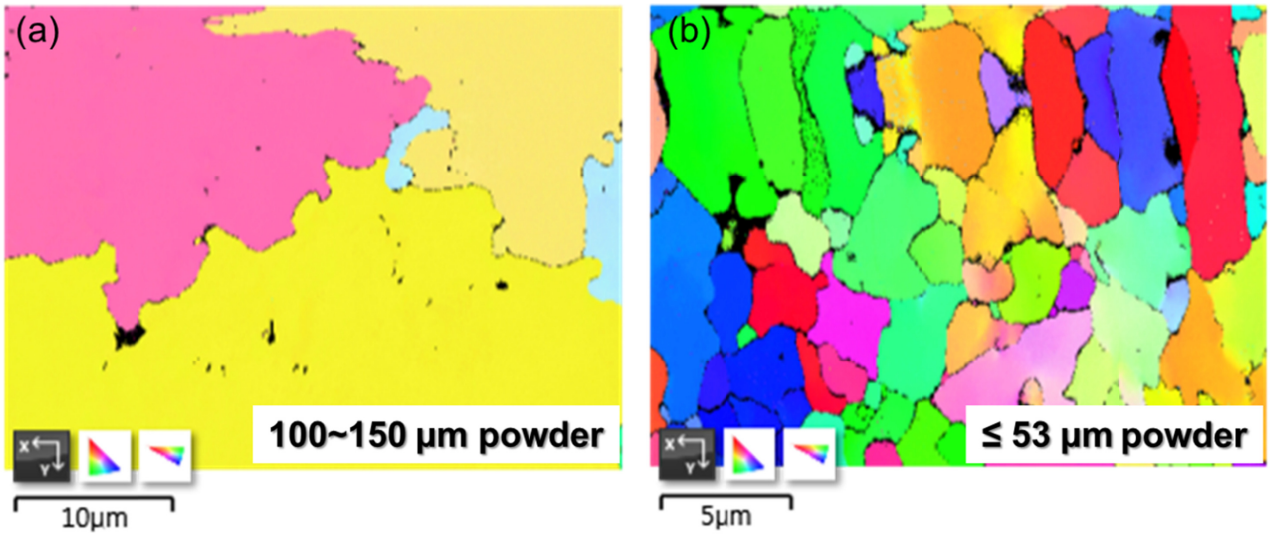

Fig. 4. Cross-sectional EBSD images of the atomized powders (a) 100~150 μm large sized powder, (b) <53 μm small sized powder

It was confirmed by the XRD data of the sintered samples that there was no carbon contamination induced second phase or phase separation during sintering at elevated temperatures up to 1000°C (Fig. 5). In addition, it was difficult to estimate the relative density due to lack of accurate reference in the case of density of the alloy, but it was confirmed that the maximum density was obtained at 900°C (7.455 g/cm^3), and it was maintained at 1000°C (7.493 g/cm^3). Furthermore, Vickers hardness of the sintered body decreased at 1000°C sintering temperature (Fig. 6(a)); the optimum SPS sintering temperature was determined to be 900°C in this study.

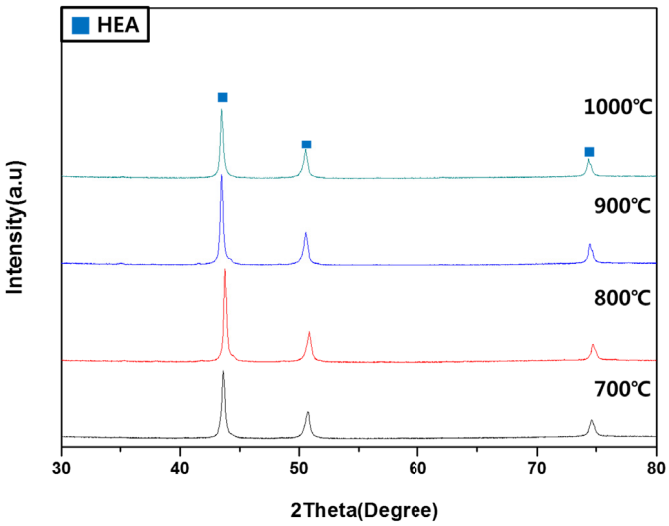

Fig. 5. XRD analysis of the SPS sintered CoCrFeNiMn HEA

Vickers hardness was measured for characterization of mechanical property of sintered body of atomized powder. In order to obtain the optimum density and hardness value at 900°C, those properties were measured while increasing the holding time in 2 minutes increments. The density of the sintered specimens reached the maximum at 8 min holding time (7.747 g/cm^3), and it was maintained at 10 min sintering condition at 900°C (7.742 g/cm^3). The Vickers hardness showed a maximum value of 408.06 hv at 8 min holding time and decreased to 344.1 hv when the holding time was increased to 10 min (Fig. 6(b)). It seemed that the full density was obtained at a holding time of 8 minutes, and the hardness value decreased because grain growth had occurred for an additional 2 minutes. It was assumed that the brittle secondary phase was not formed during sintering in this condition.

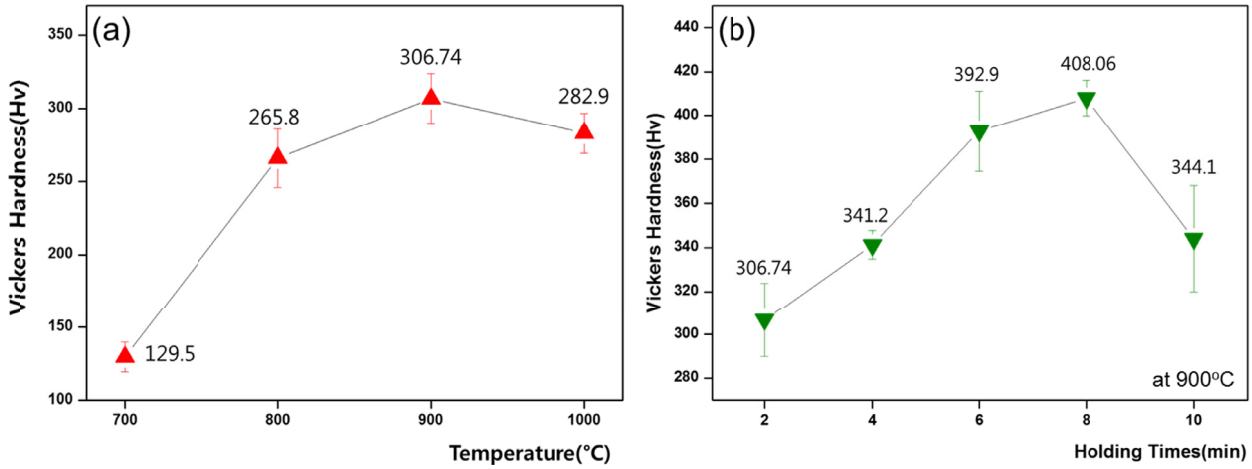

Fig. 6. Vickers hardness change of SPS sintered body (a) by the sintering temperature and (b) by the sintering time at 900°C

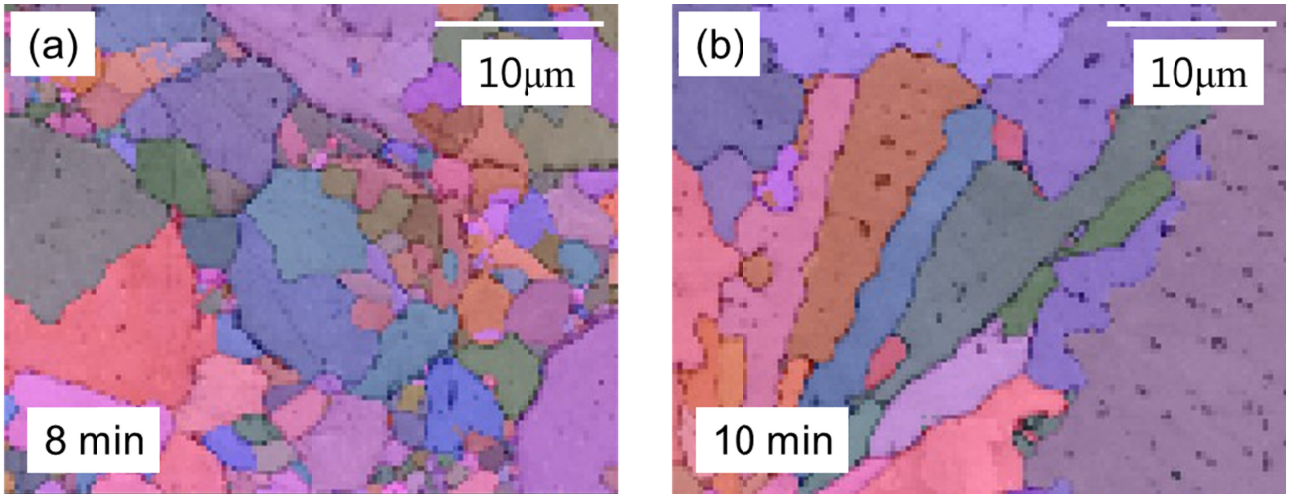

Fig. 7. EBSD images of sintered body, (a) 8 min, and (b) 10 min of sintering time

EBSD measurements were performed to demonstrate the reduction of hardness values due to grain size increment (Fig. 7). As the sintering time increased from 8 minutes to 10 minutes, the grain size increased significantly from 2.77 to 4.12 μm. It was confirmed that the Vickers hardness decreased due to grain growth. Interestingly, it was confirmed that the grain growth in HEA caused a bimodal distribution, that is, abnormal grain growth. Both 8 and 10 minutes sintered bodies with full density have a faceted and elongated grain boundary structure, which is known to induce abnormal grain growth [9,10]. It is considered that significant grain growth occured due to the abnormal grain growth. The reason of the abnormal grain growth in the SPS sintering process of the HEA powder produced by the gas atomization will be investigated through further studies.

4. Conclusions

In this study, the mass production process of the HEA powder has been studied. The gas atomization process, which can mass produce and minimize the contamination and produce spherical high quality powder, was applied and successfully in the production of the CoCrFeNiMn based HEA. 4.2 kg of HEA powder was successfully produced in one experiment, and all the powder was confirmed to form a single fcc phase. From the composition analysis by EDS, it was confirmed that the five elements were uniformly distributed in the spherical powder. The fabricated powder was sintered through SPS and showed the highest hardness values when sintered at 900°C for 8 minutes. The microstructure of the sintered body showed an abnormal grain growth.

REFERENCES

[1] J.W. Yeh, Adv. Eng. Mater. **6**, 299-303 (2004).
[2] J.W. Yeh, Ann. Chim. Sci. Des. Mater. **31**, 633-648 (2006) .
[3] N. Stepanov, Intermetallics **59**, 8-17 (2015).
[4] S.H. Joo, J. Alloys Compd. **698**, 591-604 (2017) .
[5] F. Otto, Acta Mater. **61**, 5743-5755 (2013).
[6] B. Schuh, Acta Mater. **96**, 258-268 (2015).
[7] Z. Fu, Mater. Sci. Eng. A, **644**, 10-16 (2015).
[8] Y. Liu, Intermetallics. **68**, 16-22 (2016).
[9] S.Y. Ko, J. Euro. Ceram. Soc. **36**, 1159-1165 (2016).
[10] S.J.L. Kang, J. Ceram. Soc. Jap. **124**, 259-267 (2016).