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FABRICATION OF NANO-GRAINED TiC/Ti_5Si_3 MICRO-MOLDS BY THE LIGA-MA PROCESS

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ABSTRACT

The importance of metals and ceramics are increasing to microsystem in reproduction and molding techniques because of the mechanical and physical properties. In this study, we have developed a new process using LIGA mold which is able to cast a microstructure of alloys or ceramics using Spark Plasma Sintering (SPS) machine. Concretely, we apply the mechanical alloying (MA) process as well as a pseudo-superplasticity to produce micro-mold made of these composites. Powders of elements Ti and SiC whose composition was Ti-20mass%SiC were blended for MA, and the MA powder whose average particle size is less than 1 μm, i.e., nano-particle, has an amorphous structure. The MA powder is filled into a micro-mold produced by LIGA process, and cast together by SPS in order to fabricate a new micro-mold as a transcription of the micro-mold by LIGA process. As the result, this process proved successful for making the micro mold made by the TiC/Ti_5SiC_3 ceramic composites, whose Vickers hardness is extremely superior to Ni mold produced by general LIGA process.

Keywords ; MA, SPS, LIGA, TiC, Ti_5Si_3, Powder metallurgy, Pseudo-superplasticity

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INTRODUCTION

Recently, a miniaturization and integration in micro-fabrication technology is progressing by an increasing requirement of industrial development. Specially, many kinds of micro-parts with a high aspect ratio has been fabricated by Lithographie-Galvanoformung-Abformung (LIGA) process using deep-X ray lithography, electroforming and molding [1]. Generally, the micro-parts fabricated by the LIGA process are used for a micro-mold in reproduction techniques such as a powder injection molding [2]. However, the micro-molds are now made of a limited number of materials such as polymers, Ni, Au, Cu and Ni-Co alloys, which are relatively soft and have a lower melting temperature to use as the mold [3]. In order to produce a new functional Micro Electro Mechanical Systems (MEMS) parts, it is important to develop novel material for the LIGA process. In this term, ceramics are suitable as material for the micro-mold, though they have poor formability. Meanwhile, one of the authors has reported that a TiN/Ti_5SiC_3 and a TiC/Ti_5SiC_3 ceramic composites produced by mechanical alloying (MA) process have microstructure consisting of amorphous and nano alpha-Ti phases [4]. These composites indicated a pseudo-superplasticity under the some specific condition of temperatures and strain rates.

In the present study, we apply the MA process as well as the pseudo-superplastic deformation to produce micro-mold made of a TiN/Ti_5SiC_3 and a TiC/Ti_5SiC_3 composites. Concretely, the MA powder is filled into a micro-mold fabricated by LIGA process, and cast together by Spark Plasma Sintering (SPS) in order to fabricate a new micro-mold as a transcription of the micro-mold by LIGA process. Firstly, powders of elements Ti and SiC or Si_3N_4 whose composition was Ti-20mass%SiC or Ti-20mass%Si_3N_4 were blended for MA, and the microstructure of these MA powders is examined by means of X-ray diffraction (XRD) analysis. Then the MA powders were sintered with micro-mold made by LIGA process at several sintering temperatures. The sintered products were investigated by SEM.

EXPERIMENTAL PROCEDURE

This process consists of 4 steps; 1) compounding different metal powders and form a homogeneous alloy powder using MA, 2) fabrication of a Ni structure as a mold by general LIGA process, 3) sintering together the Ni mold and the alloy powder by SPS, 4) polishing the sintered product and etching only the Ni mold, then, final product is obtained. The detail of each step is explained as follows.

Fabrication of alloy powder

The starting materials were a commercially pure Ti (99.7 mass%) powder of average particle size of 45 μm, SiC (99.2 mass%) powder of average particle size of 9.4 μm and an α–Si_3N_4 (98.7 mass%) powder of average particle size of 720 nm. They were blended to the composition of a Ti-20 mass% SiC and a Ti-20 mass% Si_3N_4 respectively, and mechanically alloyed by a planetary ball mill conducted at a rotating speed of 250 rpm for 720 ks with a SKD11 vial and SUJ2 balls under an Ar gas atmosphere. The powder to ball weight ratio was 1 : 7.2. During the milling, 0.5 mass% of n-Heptane was added as a process control agent.
The MA powders were examined by XRD and SEM.

Fabrication of Ni mold

The LIGA process can fabricate microstructures with a high aspect ratio of more than 100, corresponding to less than several microns in width and more than several hundred microns in height, because of the high directivity X-rays from the synchrotron radiation (SR) source [1]. The process is shown in Figure 1. A pattern of an X-ray mask is transcribed by an exposure using X-ray from SR source to PMMA resist which is formed on Si wafer. The exposed area of PMMA resist is soluble in a developer because the X-ray distributes molecular chains of exposed area. Therefore, after development, same pattern with the X-ray mask remains on the Si wafer as a pressed structure made by PMMA. Finally, the PMMA structure is electroplated and separated from Si wafer. As shown these steps, the elements of LIGA process is classified broadly into three categories; deep-X ray lithography, electroforming and molding. In particular, a fabrication technique of X-ray mask is the most important because a precision of the final structure depend on that directly. Each process described above require many essential technique to be described, although the details are omitted from this paper (see ref. [5] for detail). Figure 2 shows SEM image of the Ni mold of the microstructure, 200 μm in thickness and the minimum space in the mold is 80 μm.

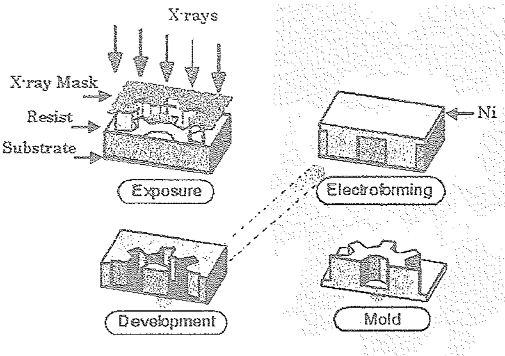

Fig. 1 A schema of the LIGA process

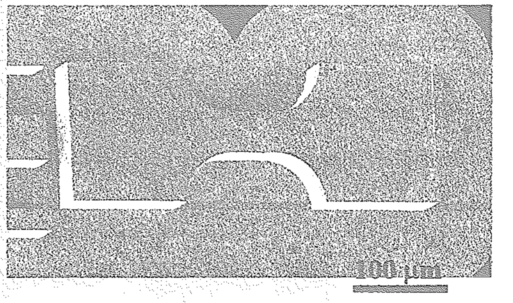

Fig. 2 SEM image of the Ni mold of the microstructure, 200 μm in thickness.

Sintering by SPS

The MA powders are sintered by SPS at several temperatures. A SUMITOMO SPS-510L was used for sintering of powders with graphite die(ϕ30/ ϕ15x30) and punch(ϕ 15x20). Before filling of the powder and Ni mold, a BN was sprayed to inside of the graphite die in order to pull the product out after sintering. The MA powder of 2.0 g and Ni mold were packed and sintered under an atmosphere of 15 Pa.

Polishing and etching

The sintered product was polished and etched by nitric acid at 303 K whose concentration is 30 % in order to get rid of the Ni mold.

RESULTS AND DISCUSSION

Figures 3 show SEM images of the MA powders of Ti-20mass% SiC in (a) and Ti-20 mass% Si_3N_4 in (b) respectively after 720 ks milling adding 0.5 mass% of n-Heptane. As shown in the figure, the average particle sizes of 1 μm of Ti-20mass% SiC is smaller than that of 10 μm of Ti-20 mass% Si_3N_4. Specially, the MA powder of Ti-20mass% SiC adding 1.0 mass% of n-Heptane was produced. A SEM image of the MA powder is shown in Figure 4. The figure indicates an average particle size is less than 1 μm. Smaller particle size gets lower a sintered temperature of SPS and fabricates more compact mold. Therefore, the MA powder of Ti-20mass% SiC adding 1.0 mass% of n-Heptane is selected as a material of micro-mold. On the following of this paper, the MA powder indicates that of Ti-20mass% SiC adding 1.0 mass% of n-Heptane.

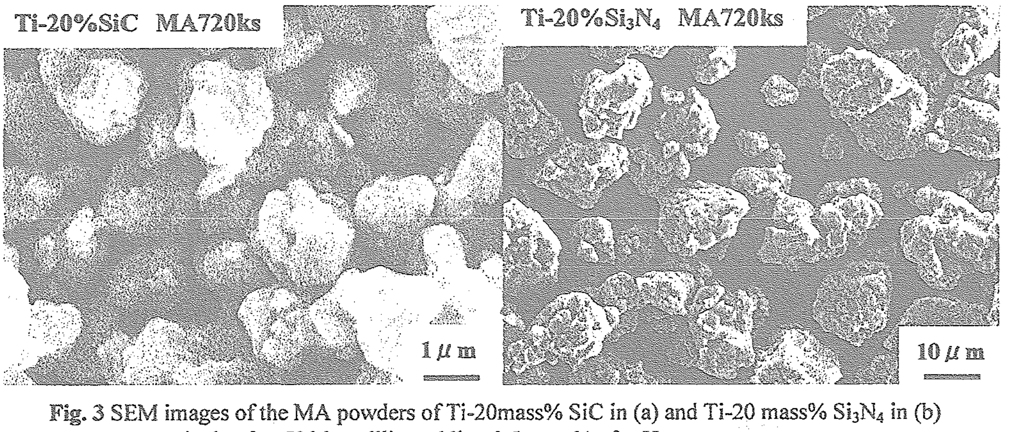

Fig. 3 SEM images of the MA powders of Ti-20mass% SiC in (a) and Ti-20 mass% Si_3N_4 in (b) respectively after 720 ks milling adding 0.5 mass% of n-Heptane.

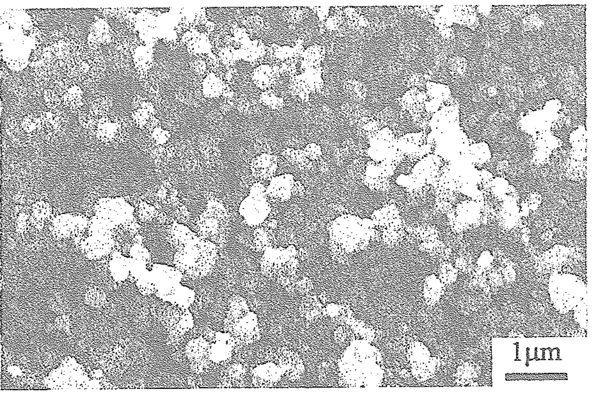

Fig. 4 SEM image of the MA powders of Ti-20mass% SiC after 720 ks milling adding 1.0 mass% of n-Heptane.

Before filling the MA powder into the Ni mold, only the MA powder is sintered at several sintering temperatures by SPS in order to investigate the microstructure of the SPS composite. The microstructure change depending on sintered temperature was examined by means of XRD analysis. Figure 5 shows XRD patterns using Cu Kα radiation of the MA powder sintered at 773 K, 873 K, 973 K, 1073 K and 1173 K with original MA powder. Substantial broadening of the XRD peaks of the original MA powder changed along with the raise of sintering temperature. XRD peaks of a TiC and Ti_5Si_3 phase appeared conspicuously at 1073 K and 1173 K. This indicates that the original MA powder has an amorphous structure, and precipitation of TiC and Ti_5Si_3 phase begin from 1073 K of sintering temperature. In terms of casting the MA powder into the micro-mold, the amorphous structure is suitable because the MA powder will be crystallized during the cast and the crystallization cause a heavy plastic deformation without any stress concentration, i.e., pseudo-superplasticity. The phenomenon work as good effect for high densification and accuracy of micro-mold. As the results of XRD, the MA powder is cast with Ni mold by SPS at 973 K which is the highest temperature with keeping the amorphous structure, and then held at several temperatures for high densification.

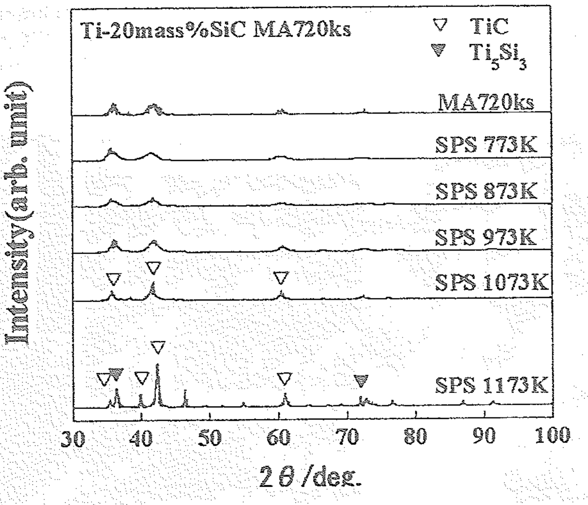

Fig. 5 XRD patterns of the MA powder sintered at 773 K, 873 K, 973 K, 1073 K and 1173 K with original MA powder.

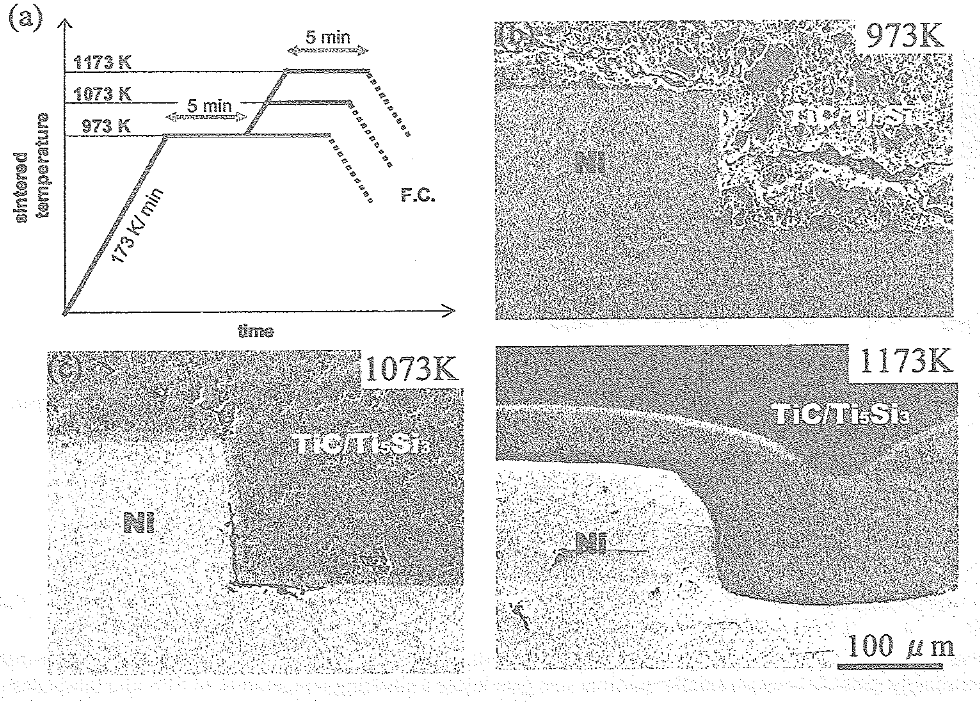

Fig. 6 (a) a diagram of SPS sintering process and SEM images of the microstructure of the compacts sintered at 973 K (b), 1073 K (c) and 1173 K (d) after keeping at 973 K for 5 min.

Figure 6(a) shows a diagram of SPS sintering process. The microstructure of the compacts sintered at 973 K, 1073 K and 1173 K after keeping at 973 K for 5 min are examined by SEM. The results are shown in Figure 6(b), (c) and (d). The TiC/Ti_5SiC_3 ceramic composites at 973 K in (b) were crumbled during polishing of the specimen because sticking of each MA powder was not enough. On the other hand, at 1173 K in (d), some phase were appeared around the Ni mold, whose thickness is over 50 μm. This phase are precipitated from Ni mold because of a distribution of Ni atom at this temperature. As the results, the sintered temperature of 1073 K in (c) is suitable by comparing the others.

Figure 7 shows SEM images of the TiC/Ti_5SiC_3 ceramic composites mold for a tensile test peace after etching of Ni mold. As shown in this figure, the structure of the micro mold has not a sharp edge. This happened during etching of the Ni mold. However, as shown in Figure 8, an average of a Vickers hardness comparing between the Ni mold by LIGA process and TiC/Ti_5SiC_3 ceramic composites mold by this process. The hardness of the TiC/Ti_5SiC_3 ceramic composites is superior to that of Ni.

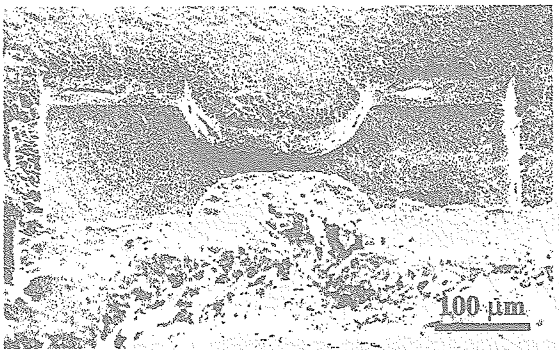

Fig. 7 A SEM image of the TiC/Ti_5SiC_3 ceramic composites mold.

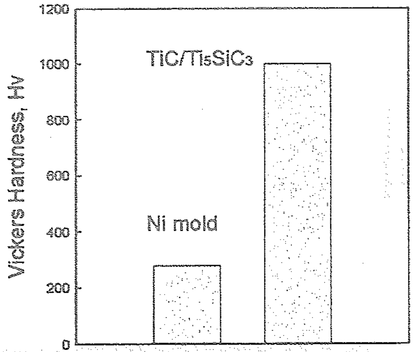

Fig. 8 a Vickers hardness comparing between the Ni mold by LIGA process and TiC/Ti_5SiC_3 ceramic composites mold.

CONCLUSIONS

In the present study, we apply the MA process to produce micro-mold made of a TiN/Ti_5SiC_3 and TiC/Ti_5SiC_3 composites, and it was found as a following.

The average particle size of Ti-20mass% SiC adding 1.0 mass% of n-Heptane is less than 1 µm, i.e., nano-particle. This is extremely suitable because smaller particle size gets lower a sintering temperature of SPS and fabricates more compact mold. Moreover, the microstructure of the MA powder has an amorphous structure at under 973 K of sintering temperature. Because the crystallization during the cast make deformation stress down, it works as good effect for high densification and accuracy of micro-mold. For next step of this study, we attempt to find out an evidence of the appearance of pseudo-superplasticity by observation using transfer electron microscope.

As the result, although we have to improve the etching process of Ni mold, this process proved successful for making the micro mold made by the TiC/Ti_5SiC_3 ceramic composites, whose Vickers hardness is superior to that of Ni mold by general LIGA process. Therefore, it is expected that the LIGA-MA process is effective technique and will be applied to practical and high performance MEMS parts or mold for injection molding and powder injection metallurgy.

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