Influence of Cu-Y Compound Content on the Microstructure of Cu-Y$_2$O$_3$ Dispersion Strengthened Alloys Synthesized by MA and HIP Process[*]

Bing MA[1], Yoshimitsu HISHINUMA[1,2], Hiroyuki NOTO[1,2] and Takeo MUROGA[1,2]

[1]*The Graduate University for Advanced Studies, SOKENDAI, Toki 509-5292, Japan*
[2]*National Institute for Fusion Science, Toki 509-5292, Japan*

Oxide Dispersion Strengthened Cu alloy (ODS-Cu) with Y$_2$O$_3$ has great application potential in the field of fusion. In the previous fabrication method by adding metal Y as the source of Y$_2$O$_3$, severe sticking occurred during mechanical alloying (MA) and huge Y particles still remained after MA. Considering that Cu-Y compounds are more brittle than pure Y, which is expected to resolve the sticking issue, and have lower Y enrichment, which will make it easier to form uniform Y distribution, ODS-Cu with various content of Y by adding Cu$_2$Y or Cu$_6$Y were fabricated through MA and Hot isostatic pressing (HIP) process. A comparative analysis was made for the samples with addition of Cu$_2$Y and Cu$_6$Y. The results showed that, compared with Cu$_2$Y, Cu$_6$Y is easier to form uniform Y distribution. The most likely reason is that the Cu$_6$Y is more brittle and less Y abundance than Cu$_2$Y. The sample with 0.39 wt% Y with Cu$_6$Y addition has the highest Vickers hardness, possibly because of solution strengthening caused by higher content of interstitial O, and better electrical conductivity than the sample with 1.19 wt% Y with Cu$_6$Y possibly because of the more uniform formation of Y$_2$O$_3$ and the absence of precipitation phases.

1. Introduction

As a critical component of fusion device, divertor plays an important role in extracting heat and ash produced by the fusion reaction, and minimizing plasma contamination. The extreme service environment requires both excellent thermal conductivity and mechanical properties for the heat sink material. Cu based materials with excellent thermal conductivity were chosen as the primary candidate heat sink materials. Among them, many kinds of ODS-Cu have been developed by adding oxide particles (alumina [1], zirconia [2], yttria [3], and so on) to achieve dispersion strengthening. Among them, the mature commercial ODS-Cu with alumina (Glidcop®) has been developed by internal oxidation method [1]. ODS-Cu with yttria is the current mainstream because of the lower solubility and higher thermal stability [4]. Kudashov [5], U. Martin [6], *et al.* fabricated the ODS-Cu with Y$_2$O$_3$ through the MA process at low temperature, called "cryo-milling". Aghamiri *et al.* fabricated the ODS-Cu with Y$_2$O$_3$ particles by adding process control agent (PCA) [3]. Carro *et al.* produced the ODS-Cu with Y$_2$O$_3$ particles first by vacuum induction melting, then conventional milling and HIP [7]. Our previous works succeeded in producing the

ODS-Cu with Y$_2$O$_3$ using pure Y metal powders as the source of Y$_2$O$_3$ by mechanochemical alloying through the MA and HIP process [8, 9]. While, the severe sticking and the remains of huge Y particles indicated that fabrication process need to be further modified. Considering that the Cu-Y compounds are more brittle than pure Y, which is expected to resolve the sticking issue [10], and Cu-Y compounds have lower Y enrichment, which will make it easier to form uniform Y distribution, Cu-Y compounds were selected as the source of Y$_2$O$_3$ as well as process control agents to fabricate the ODS-Cu with Y$_2$O$_3$.

In this study, in order to develop the heat sink material for divertor, two kinds of Cu-Y compound (Cu$_2$Y and Cu$_6$Y) were used as the Y source to fabricate the ODS-Cu with different Y content by MA and HIP process. A comparative analysis was made for samples by adding Cu$_2$Y and Cu$_6$Y, and the influence of Y content was also explored.

2. Experiment Procedure

Two kinds of Cu-Y intermetallic ingot (Cu$_2$Y and Cu$_6$Y) were prepared by pure Cu (99.99%, purity), and Y (99.9%, purity) through arc-melting in high-purity Ar atmosphere. Several times of arc-melting were conducted to make the homogeneous Cu-Y compound buttons, followed by heat-treatment at 600°C for 100 hr in a vac-

---

Table 1   The composition of ODS-Cu- x wt % Y.

	Cu(g)	Cu$_2$Y(g)	Cu$_6$Y(g)
Cu-0.39 wt %Y (Cu$_2$Y)	99.40	0.96	-
Cu-0.39 wt %Y (Cu$_6$Y)	97.92	-	2.08
Cu-1.18 wt %Y (Cu$_2$Y)	97.13	2.87	-
Cu-1.18 wt %Y (Cu$_6$Y)	93.75	-	6.25
Cu-2.36 wt %Y (Cu$_2$Y)	94.26	5.74	-
Cu-2.36 wt %Y (Cu$_6$Y)	87.51	-	12.49

uum condition, and crashing to form fine powders. The Cu-Y fine powders were confirmed by thermogravimeter-differential thermal analyzer (TG-DTA) and XRD in previous work [11].

ODS-Cu with various content of Y from 0.39 wt% to 2.36 wt% were prepared, and the compositions were shown in the Table 1. The mixed powders were milled for 32 hr with a speed of 250 rpm through planetary-type ball mill machine (Pulverisetee 5, Fritsch) in Ar atmosphere. The diameter of stainless steel ball used for the MA was 5 mm and the ball-powder ratio was 7:3, which were selected based on previous works [9]. The milled powders were put into the steel capsules. Before clamping, the capsules were degassed for 1 hr in 0.1 Pa vacuum, followed by welding in the vacuum condition. During the HIP process, the steel capsules, filled with milled powders, were kept in the pressure of 150 MPa at temperature of 1000°C for 2 hr.

The milled powders with different MA time and the bulk samples after HIP were analyzed by XRD, morphological observation. Finally, the bulk samples after HIP were evaluated in the terms of thermal conductivity and mechanical properties, which are the most important parameters for heat sink materials. As to the mechanical property, Vickers Hardness test was chosen because it is an important means for rapid quality assessment. As to thermal conductivity, it is mainly dominated by phonon conduction, and there is a close relationship between the electronic and thermal conduction on each Cu grains, so electrical resistivity measurement is a one of the simple methods to evaluate thermal conductivity.

The XRD analysis were conducted on the Rigaku RINT-2200 diffractometer with Cu Kα radiation with the parameters of 40 kV and 40 mA. Based on the XRD data, lattice parameters were calculated by Bragg's Law [10], shown as follows;

$$2d \sin\theta = n\lambda, \tag{1}$$

where θ is the scattering angle, d is the interplanar distance, n is a positive integer and λ is the wavelength of X-ray. For the Cu with FCC structure, the lattice parameter d can be presented in the following relationship;

$$d = a\sqrt{h^2 + k^2 + l^2}, \tag{2}$$

where a is the lattice parameter, and h, k, l, are the miller indices of the Bragg plane.
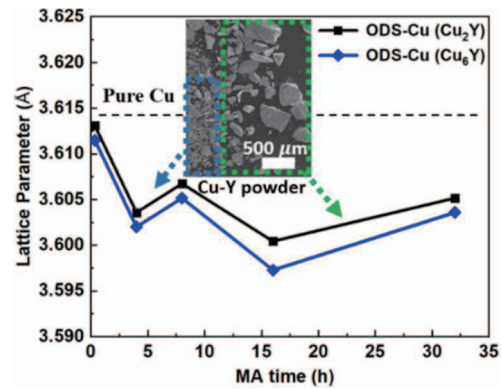

Fig. 1   Lattice parameter development with MA time for the samples with 1.18 wt% Y.

Microstructures were examined by scanning electron microscopy (SEM, JEOL JSM-5600) equipped with energy dispersive X-ray spectroscope (EDX). The Vickers Hardness were tested at room temperature with a loading of 500 gf for 30 s. The electrical conductivity measurements were conducted by four-terminal sensing method from −196°C to room temperature with current of 1, 3, and 5 A.

3. Results and Discussion
3.1   Characterization of the MA powders

Figure 1 shows the development of lattice parameters of Cu as a function of MA time for the sample with 1.18 wt% Y by adding Cu$_2$Y or Cu$_6$Y, calculated by Bragg's law shown as above. It was found that the lattice parameters of Cu for the both samples had similar macro trends, first decreasing from the original lattice parameter (3.6147Å) of pure Cu [12], then increasing from the middle MA process. The decrease during first half process is mainly due to the dominance of crystal distortion caused by the collision between MA powders and steel balls, and the subsequent increase during the latter half process is due to the solid solution dominance. It is worth noting that there is a small fluctuation during the first half process. It is probably caused by the preferential solid solution of the fine Cu-Y powders. Most of the coarse Cu-Y powders were thought to be first broken into fine powders during the early MA process, then dissolved into the Cu matrix during the latter MA process.

Figure 2 shows the development of microstructures obtained by scanning electron microscopy in backscattered electron (SEM-BSE) mode for MA powders, and the corresponding Y distribution, with MA time for the sample adding Cu$_6$Y. After 4 hr MA, the Cu-Y compounds were cracked from the initial average size of 200 μm to 20 μm, confirmed by the EDX mapping of Y element. With the increase in MA time, the Cu-Y compounds were further cracked into several μm. After 32 hr MA, the Y were uniformly dissolved into Cu matrix.
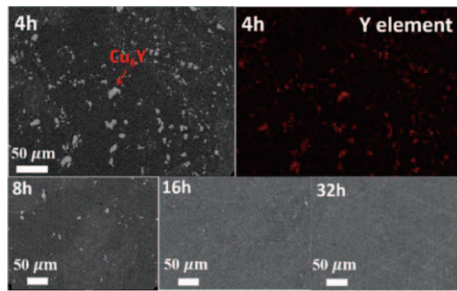
Fig. 2   Microstructure and the EDX mapping of MA powders from 4 to 32 h for the sample with 1.18 wt% Y.
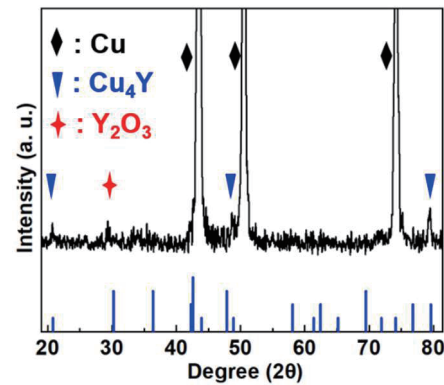

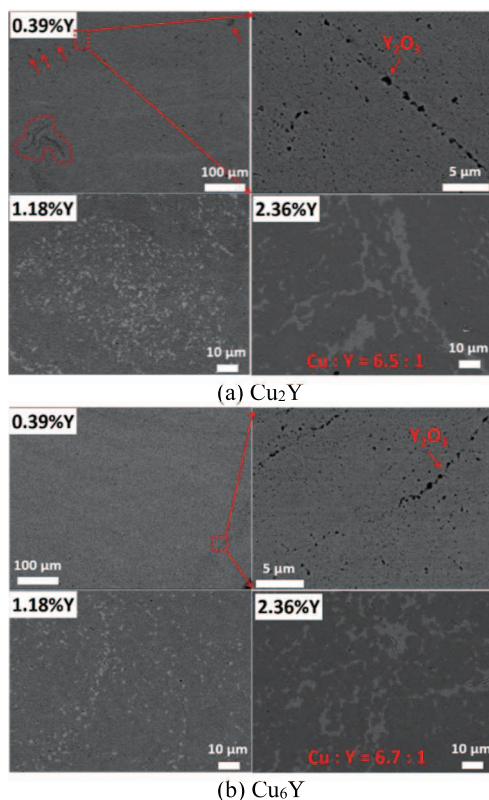(a) Cu_2Y

(b) Cu_6Y

Fig. 3   SEM-BSE images of the bulk samples with various Y content by adding Cu_2Y (a) and Cu_6Y (b).

3.2   Characterization of the consolidated bulks

Microstructures of the bulk samples after HIP with various Y content (from 0.39 wt% to 2.36 wt%) by adding different Cu-Y compounds are shown in Figs. 3 (a) by adding Cu_2Y and (b) by adding Cu_6Y. For the sample with lower content of Y using Cu_2Y, the Y_2O_3 particles with largest size of 1 μm were formed after HIP. Considering no oxidant was introduced and Ar gas protection was conducted during fabrication process, the oxygen element in sintered materials possibly came from the inherent O impurity in the initial raw materials or was introduced during the transfer process. It should be highlighted that there still have some Y enrichment areas labeled by red circle and arrows. For the samples with 1.18 wt% and 2.36 wt%

Fig. 4   XRD spectra of the sample with 1.18 wt% Y (Cu_6Y).

Y, there are plenty of phases with light color in the SEM-BSE images, and it was found that these phases showed a aggregated state with Cu:Y ratio of 6.5:1 confirmed by EDS.

In case of the bulk sample by adding Cu_6Y with lower Y content, Y_2O_3 particles with similar size were also formed after HIP. Different from the sample by adding Cu_2Y, the sample with Cu_6Y is much more uniform, and there is no Y enriched area, observed in the sample adding Cu_2Y. Cu_6Y is beneficial to form the uniform Y distribution. For the sample with higher content of Y, the similar aggregation was observed, and there is no clear difference between the samples with higher content of Y by adding Cu_2Y or Cu_6Y.

Figure 4 shows the black XRD spectra of the bulk sample with 1.18 wt% Y by adding Cu_6Y and blue standard spectra of Cu_4Y compound. The main peaks labelled by black diamond are the characteristic peaks of Cu, and the small specific peak of Y_2O_3 labeled by red star corresponds to the fine Y_2O_3 particles shown in the SEM-BSE images. The specific peaks of Cu_4Y for the bulk samples indicated that the aggregated phases shown in the SEM images are Cu_4Y compounds. The mismatch between the experimental data and the standard data for the major peaks of Cu_4Y were caused by the influence of adjacent Cu peaks and the different grain orientation of Cu_4Y compound. The higher ratio of Cu:Y (~6.5:1) than Cu_4Y obtained by EDX was considered to be caused by the influence of Cu background.

Based on the Cu-Y phase diagram [11], phase transformation occurred for Cu_6Y compound at 886°C and it was melted at 927°C. The MA powders had uniform Y distribution after ball milling, and the Cu:Y ratio was diluted to around 100:1. During HIP process at 1000°C, the Cu-Y phases were melted, forming liquid phase, and then aggregated to increase the ratio of Cu:Y in the aggregated zone, followed by precipitation initiated at 971°C in the form of Cu_4Y compound during the cooling process.

3.3   Performance evaluation

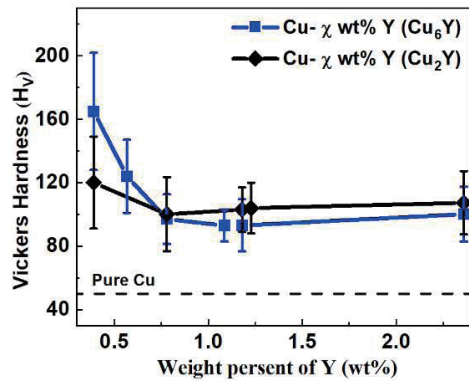Figure 5 shows the influence of Y content on the Vick-

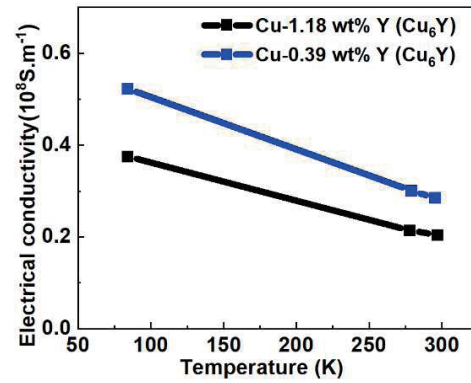Fig. 5 Vickers hardness of Cu- x wt% Y (Cu_2Y or Cu_6Y).

Fig. 6 Electrical conductivity of Cu- x wt% Y (Cu_6Y).

ers hardness for the samples by adding Cu_2Y or Cu_6Y. Compared with pure Cu, Vickers hardness was greatly improved by adding Cu-Y compound, because of the formation of Y_2O_3 particles. For the samples with Cu-Y compound, the Vickers hardness gradually decreased and reached saturation with the increase of Y content. The inherent interstitial O have great influence on the Vickers hardness of ODS-Cu, and the decrease of Vickers hardness with the increase in Y content is possibly because the redundant of Cu-Y consumed all of the interstitial O impurity. Besides, the precipitated macro phases distributed in the Cu matrix had small influence on the Vickers hardness. That is also the reason that Vickers hardness does not change with the increase of Y content from 1 wt%. The sample with 0.39 wt% Y (Cu_6Y) has higher Vickers hardness than the sample with 0.39 wt% Y (Cu_2Y) because of more evenly distribution of Y as shown in the SEM-BSE images. For the samples with higher Y content, there is no difference in Vickers hardness between samples adding Cu_2Y and sample adding Cu_6Y, corresponding to the similar microstructure shown in the SEM-BSE images above.

Considering the better performance of the samples by adding Cu_6Y. The electrical conductivity tests were conducted only for the samples by adding Cu_6Y. As shown in Fig. 6, compared with the sample with 1.18 wt% Y, which has a large amount of Cu_4Y precipitation phase, the sample with 0.39 wt% has better electrical conductivity, phase possibly because of the more uniform formation of Y_2O_3 and the absence of precipitation phases. Combing with the Vickers hardness, the sample with lower content of Y by adding Cu_6Y has better comprehensive performance.

4. Conclusions

ODS-Cu with various content of Y by adding Cu_2Y and Cu_6Y were fabricated through MA and HIP process. A comparative analysis was made for samples by adding Cu_2Y and Cu_6Y, and the influence of Y content was explored. The results show that, compared with Cu_2Y, Cu_6Y is easier to induce uniform Y distribution, because of lower Y abundance and higher brittleness of Cu_6Y. The sample with 0.39 wt% Y with Cu_6Y addition has the highest Vickers hardness, possibly because of the solution strengthening caused by higher content of inherent interstitial O, and better electrical conductivity than the sample with 1.18 wt% Y with Cu_6Y because of without precipitation phase possibly because of the more uniform formation of Y_2O_3 and the absence of precipitation phases.

Acknowledgement

[1] Brochure GlidCop® Copper Dispersion Strengthened with Aluminum Oxide, SCM Metals Products, Inc., *Research Trianplc Park*, NC (1994).
[2] M.S. Abd-Elwahed *et al.*, Ceramics International **46**, 56 (2020).
[3] S.M.S. Aghamiri *et al.*, Nucl. Mater. Energy **15**, 17 (2018).
[4] M.M. Li *et al.*, *Comprehensive Nuclear Materials (Second Edition)* **6**, 93 (2020).
[5] D.V. Kudashov *et al.*, Mater. Sci. Eng. A, **387-389**, 768 (2004).
[6] U. Martin *et al.*, WIT Trans. Built. Environ. **6**(7), 341 (2004).
[7] G. Carro *et al.*, Fusion Eng. Des. **138**, 321 (2019).
[8] B. Huang *et al.*, Nucl. Mater. Energy **16**, 168 (2018).
[9] B. Ma *et al.*, Nucl. Mater. Energy **24**, 1007732 (2020).
[10] D. Alderton *et al.*, X-Ray Diffraction (XRD), *Encyclopedia of Geology*, 2nd edition 2020.
[11] B. Ma *et al.*, Fusion Eng. Des. **161**, 112045 (2020).
[12] M.E. Straumanis *et al.*, Acta Crystallogr. **A25**, 676 (1969).