氏　　名　MA Bing

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学 位 論 文 題 目　MA-HIP processing of yttria dispersion strengthened copper alloys for fusion application

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(Form 3)

Summary of Doctoral Thesis

Name in full MA Bing

Title MA-HIP processing of yttria dispersion strengthened copper alloys for fusion application

As a promising candidate for heat sink material of the diverter, which is expected to operate in an extreme environment with high heat flux and high irradiation damage, the oxide dispersion strengthened Cu (ODS-Cu) alloy exhibits a remarkably high strength and irradiation resistance. Compared to the commercial ODS-Cu alloy with Al_2O_3 particles (Glidcop®), the ODS-Cu alloy with Y_2O_3 particles has potential advantages because of the higher enthalpy of the Y_2O_3 formation, which is beneficial to thermal stability, and the lower solubility of Y in Cu matrix, which is beneficial to thermal conductivity. While, low solubility of Y leads to unacceptable to apply the conventional internal oxidation method, which is used to fabricate Glidcop®. The main way to fabricate the ODS-Cu alloy with Y_2O_3 must use a different process from the internal oxidation method, such as the mechanical alloying and hot isostatic pressing (MA-HIP). During the conventional MA-HIP process, the Y_2O_3 originated from the external addition is still remained larger size after HIP. These Y_2O_3 particles are thermodynamically unstable and easily aggregable. Considering the fine dispersive particles with a high number density is the key factor in developing highly strengthened ODS-Cu alloys, the objective of this doctoral thesis is developing the several processes to enhance the Y distribution, to refine the dispersive Y_2O_3 and to reduce the Fe impurities.

In this thesis, an innovative MA-HIP process by an in-situ fabrication method was developed, in which Y_2O_3 particles were formed in-situ by a chemical reaction between the Y precursor and the O element. The in-situ formed dispersive particles are expected to be finer and thermodynamically stable, which can improve the mechanical strength under higher temperate and neutron irradiation. Based on this innovative MA-HIP process, the ODS-Cu alloys with in-situ formed Y_2O_3 particle were fabricated through the chemical reaction using the pure metal Y and the Cu-Y compounds. Especially, Cu-Y compounds with lower Y enrichment are brittle and they can expect to distribute homogeneously during the MA. For the comparisons, the ODS-Cu alloy with Y_2O_3 from the external addition was also fabricated by the conventional MA-HIP process. The influence of fabrication parameters (HIP temperature from 850 °C to 950°C, MA time from 32 h to 96 h) on the Y distribution, and size evolution of the MA powders were investigated based on pure metal Y sourced ODS-Cu. The influence of different Y_2O_3 sources (direct Y_2O_3, pure metal Y and Cu-Y compounds such as Cu_2Y and Cu_6Y) on

Y_2O_3 distribution and Fe impurities were also investigated.

For the influence of HIP temperature from 850 °C to 950 °C, the diffusivity of Y and O in the Cu matrix was increased with increasing temperature, promoting the in-situ formation of Y_2O_3 at high temperature. In addition, the increasing HIP temperature decreased the number density of the micro holes, corresponding to the increase in relative density from 95.8 % to 98.9 %. The higher HIP temperature is effective to enhance the in-situ formation of Y_2O_3 and decrease the porosity of ODS-Cu.

For the influence of MA time from 32 h to 96 h, it was found that extending of the MA time enlarged the lattice parameter of MA powders from 3.596 Å to 3.6158 Å. This means that the increase amount of Y solid solubility, resulting in the increase in Vickers hardness of MA powders from 100 Hv to 380 Hv. The extending of the MA time can enhance the uniform each element distribution, while introducing more Fe impurities because of the abrasion between MA powders and grind mediums.

For the size evolution of MA powders, the coarse MA powders ($d > 200$ μm) with a shell structure was formed and occupied the 80 wt. % of all MA powders. The shell of coarse MA powders had a larger Vickers hardness of 325 Hv and a higher oxygen content of 20 at. %, similar to the finer MA powders. On the other hand, the central area region of the coarse MA powders had a atomic ratio of Y and O being 2:3, same as the atomic ratio of Y_2O_3. Combing the morphology by SEM and diffraction patterns by TEM, the peeled O rich fragments from the surface of the coarse MA powders were main source of finer MA powders with oxide-like microstructures. This oxide-like O-rich fragment gave the great influence on the thermal conductivity. Therefore, the screening the alloyed MA powders before HIP treatment is an effective way to improve the thermal conductivity of the ODS-Cu alloy.

For the Cu-Y sourced ODS-Cu without oxidant, the Y distribution of the Cu_6Y sourced sample was more uniform than that of the Cu_2Y sourced sample at a lower Y content (0.39 wt.%). The XRD results and thermodynamic analysis showed that Y_2O_3 was successfully formed by the oxidation between Y and the desorbed O impurity from the Cu matrix. The Cu-Y compounds can improve the purity of the Cu matrix. This method can expand the source material selection of dispersive particles for the ODS-Cu fabrication using Cu-containing intermetallic compounds. On the other hand, the most of the unoxidized Y was aggregated and precipitated during HIP for Cu-Y sourced samples with a higher Y content (2.36 wt.%). The TG-DTA results showed that the in-situ reaction temperature of Cu_6Y and Cu_2O is 847 °C, and this temperature is lower than the melting point of the Cu_6Y (927 °C). The oxidant addition is feasible and necessary to oxidize the Cu_6Y before the melting under the in-situ fabrication process.

Furthermore, the comparisons between the direct Y_2O_3 sourced sample, the pure metal Y sourced and the Cu_6Y sourced sample with oxidant were conducted using the ODS-Cu with 1.5 wt. % Y_2O_3. The fine particle sized Y_2O_3 formation using the brittle Cu_6Y compound can enhance Y dissolution and suppress the growth of MA powders.

Smaller (19±7 nm) Y_2O_3 particles with higher number density (18.0 x $10^{20}/m^3$) were formed in Cu_6Y sourced samples, compared to the direct Y_2O_3 sourced sample with larger (73±33 nm) Y_2O_3 particles having lower number density (2.5 x $10^{20}/m^3$), and the other ODS-Cu alloys in the world. The finer Y_2O_3 particles formed by Cu_6Y compound contributed to increase about 100 MPa on the estimated yield strength based on the Orowan mechanism. The estimated value had good agreement with the measured value, but there was small mismatch. This would be possibly caused by the unoxidized Y and the contamination in the Cu matrix. It should be noted that the improvement of the estimated yield strength will be expected to enhance mechanical stability under high temperature and neutron irradiation. The stable and finer Y_2O_3 particles and the interfaces between matrix and particles will act effectively as the pinning of the dislocation and the sink ability for irradiation defects. On the other hand, the Y and Cu_6Y sourced samples through the in-situ fabrication method had more Fe impurities, because of the oxidation of milling balls by O-rich layers, which are formed when oxidant was added in the middle of the MA process. More Fe impurities increased and hardened the surface layer of MA powders, introducing holes, thereby deteriorating the elongation of the ODS-Cu.

In order to suppress the introduction of Fe impurities, reducing the Y_2O_3 content from 1.5 wt. % to 0.5 wt. % for Cu_6Y sourced samples with an oxidant was carried out. It was found that the sample with 0.5 wt. % Y_2O_3 still remained at a higher number density of Y_2O_3 ($10^{21}/m^3$), accompanied by a decrease of Y_2O_3 particle size from 19 nm to 14 nm. This is because the low concentrated solid solute Y is beneficial in forming finer Y_2O_3 during the HIP process. Furthermore, lower Y_2O_3 content decreased the introduction of Fe impurities, and reduced the thickness of the Fe accumulated boundaries and porosity, thereby improving ductility. The reducing Y_2O_3 content also improved the thermal conductivity from 68.6 % ICAS to 81.2 % ICAS, because of the forming the thinner oxide-like O rich layers and the lower Fe content impurities, which had great influence on the thermal conductivity.

Finally, it should be noted that the Cu_6Y sourced sample with a fine Y_2O_3 in high number density has a larger potential for future application once the Fe impurities and holes are reduced by modifying the grind mediums and oxidant addition. For grind mediums, the Cu coating to the steel mediums or the use of the tungsten (W) mediums are also expected to be an effective method for reducing the impurity. The W with extremely higher Mohs hardness is insoluble in the Cu matrix, which is beneficial to maintain the high purity of the Cu matrix. The pre-refining the brittle Cu-Y precursor to nano-size range is a promising method for reducing the MA time and suppressing the growth of MA powders. Besides, doping the Y_2O_3 with minor alloying elements is a candidate method to further refine the dispersive particles and increase the number density.

In my doctoral thesis, the innovative MA-HIP process of the ODS-Cu with Y_2O_3 by

an in-situ fabrication method was developed. The brittle Cu_6Y compound with a lower Y enrichment was firstly proposed as the source of Y_2O_3. Several fabrication parameters, Y_2O_3 sources and contents were investigated to enhance the uniform distribution of Y, to form finer dispersive particles and to suppress the introduction of impurities. Further improvements were also presented.

The main conclusions of my doctoral thesis are:

1. For the in-situ fabrication process, an elevated HIP temperature, a longer MA time (but introducing more impurities) and classification of MA powders can effectively enhance uniform distribution of Y and O elements, and optimize the microstructure and properties of ODS-Cu alloys.

2. Cu-Y compounds, especially the Cu_6Y compound can act as the source of Y_2O_3 and enhance the Y distribution and Y_2O_3 refinement. Besides, adding oxidant is available and necessary for an in-situ fabrication process.

3. Compared to the direct Y_2O_3 sourced sample with Y_2O_3 in a size of 73±33 nm and a number density of 2.5 x $10^{20}/m^3$, the Cu_6Y sourced sample in-situ formed fine Y_2O_3 particles 19±7 nm with a higher number density of 18.0 x $10^{20}/m^3$, but more impurities were introduced during the in-situ fabrication process.

4. Decreasing the Y_2O_3 content can refine the dispersive particles, maintain a high number density, and decrease the introduction of Fe impurities.

Form8 : Separate Sheet
（様式８・別紙１）

Results of the doctoral thesis screening

博士論文審査結果

Name in Full
氏　　名　MA Bing

Title
論文題目　MA-HIP processing of yttria dispersion strengthened copper alloys for fusion application

本論文は，将来の核融合炉に求められる高い除熱性能を有するダイバータ受熱構造体の実現に向け，その材料となる新たな銅合金の開発に関する研究をまとめたものである。一般的に純銅は他の金属と比較して圧倒的に高い熱伝導率を有する一方で，高温で機械強度が極端に低下する。加えて，核融合環境特有の中性子照射による照射軟化・硬化の問題も存在する。これらの課題解決に対して，CuCrZr 等の析出強化合金やアルミナ（Al_2O_3）を用いた酸化物粒子分散強化銅が開発されており，これらの合金は純銅に比べて良好な性質を有している。特に，Al_2O_3 粒子分散強化銅合金はすでに Glidcop という名称で製品化されているが，将来の核融合炉に対しては必ずしも十分な特性ではない。これに対し，酸化イットリウム（Y_2O_3）を用いた酸化物粒子分散強化銅合金は，Al_2O_3 を用いた場合よりも高い安定性と機械特性が期待され，現在その開発が世界的に進められている。

そこで，出願者は機械的合金化（Mechanical Alloying; MA）と熱間等方静水圧焼結（Hot Isostatic Pressing; HIP）を経由した Y_2O_3 粒子分散強化銅合金の製造方法について，従来の製造方法の問題点を明らかにし，その改善と材料としての高性能化に取り組んだ。従来の製造方法では，Y_2O_3 粉末と銅を直接 MA により合金化し，HIP により焼結体を製作しているが，焼結処理後の Y_2O_3 の凝集とそれによる Y_2O_3 粒子の粗大化が問題となっている。出願者は，銅合金内の Y_2O_3 粒子をより均質に分散させる方法として，直接 Y_2O_3 粒子を混入するのではなく，Y 元素源としての金属 Y と酸素源として銅中の溶存酸素及び酸化銅（Cu_2O）による化学的な反応を MA 及び HIP 過程で促すことを考案し，MA-HIP 処理後の銅合金中に化学的な反応によって Y_2O_3 粒子が形成されることを明らかにした。また，Y_2O_3 粒子分散した銅合金の微細組織観察及びビッカース硬度特性計測等を詳細に行い，MA 処理後の金属 Y の分散状態が合金形成後の Y_2O_3 粒子分散状態を決めていることを明らかにした。

さらに出願者は，Y_2O_3 粒子をより細粒化し，より均一に分散させるため，Y 元素源の延性・脆性に注目し，延性のある金属 Y ではなく脆性が大きい Cu-Y 金属間化合物を Y_2O_3 粒子の Y 源として用いることを試みた。その結果，世界で初めて Cu-Y 金属間化合物からの Y_2O_3 粒子生成を確認し，Cu-Y 金属間化合物から生成した Y_2O_3 粒子の分散状態は金属 Y の場合と比較して均質であることを示した。また，Cu-Y 金属間化合物の中でも脆性が大きい Cu_6Y 及び Cu_2Y 化合物の比較を行い，Cu_6Y 化合物を用いることで Y_2O_3 粒子分散状態がより均質であることを示した。Cu_6Y 金属間化合物から生成した Y_2O_3 粒子の平均粒径は 19 nm であり，これまでの Y_2O_3 粉末を用いた粒子（73 nm）や金属 Y を Y 源とした粒子（34 nm）と比較してより細粒化されていることが明らかとなった。加えて，細粒化さ

れた Y_2O_3 粒子分散した銅合金の引張強度は純銅と比較して向上していた。強度向上における粒子分散強化量は Y_2O_3 粒子の平均粒子径及び Y_2O_3 粒子の数密度を用いた Orowan モデル式に良く整合することを示し，細粒化された Y_2O_3 粒子の生成が引張強度の向上に効果的に作用したことを明らかにした。一方で，この製造プロセスでは MA 時の不純物混入が課題であることを明らかにし，この解決のために，Cu_6Y の添加量を減じることを試みたところ，減じる前に比べて明瞭に不純物が低減し，結果としてより良い機械特性と熱伝導率特性が得られた。

最後に，更なる特性改善に向けた指針として，MA 時の不純物抑制や Ti 添加が提案された。これらの実験結果は出願者独自のアイデアに基づく新しい酸化物分散強化銅合金の製造方法が，高性能の銅合金製造が可能な画期的な製造方法となる可能性を示唆するものである。

以上について出願者は，博士論文を論理的かつ明快に執筆した。研究成果は主著者として４編の査読付き英語論文にまとめられている。また主要な役割を果たした共著者として２編の論文が出版されている。申請者による研究成果は博士論文の内容として相応しく，本審査委員会は本論文が博士（学術）として十分な価値を有するものと判断した。