Cu-Ti-C Alloy Developed by Two-step Ball-milling Process

著者	WANG FENGLIN
学位授与機関	Tohoku University
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おう　ふうりん
氏　　　　　名　汪　豊林
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）材料システン工学専攻
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論 文 審 査 委 員　主査　東北大学教授　千葉　晶彦　東北大学教授　正橋　直哉
　　　　　　　　　　東北大学教授　今野　豊彦　東北大学准教授　小泉　雄一郎

論文内容要約

Copper is being widely used in industrial areas due to its high electrical and high thermal conductivities, low magnetic permeability and low elastic modulus, excellent resistance to corrosion. However, for the practical use, the inferior strength of pure copper cannot meet the design requirements of many industrial applications. Therefore, considerable attention has been paid to the development and design of novel copper-based alloys exhibiting high electrical conductivity and mechanical strength. Besides, the high thermostability during elevated temperature application is also required in some cases.

In the last decades, many studies have been carried out to design new copper-based alloys with high electrical conductivity and high strength by using precipitation- and dispersion-strengthening mechanisms. Nevertheless, it has been reported that the dispersion-strengthening is more effective in providing outstanding properties at elevated temperature compared with precipitation-strengthening as precipitates could get coarsening or dissolve into copper matrix at elevated temperature. For dispersion-strengthened copper alloys, a uniform dispersion of nanoscale dispersoids in the matrix is necessary. In-situ technique by high-energy ball-milling has been successfully applied to manufacture dispersion-strengthened copper alloys (Cu-TiC, Cu-TiB_2, Cu-NbC, Cu-Al_2O_3, Cu-ZrC). Hence, the main purpose of this research was to develop a nanoscale TiC-strengthened copper alloy which shows good combination of electrical conductivity and strength. Meanwhile, the high thermostability at elevated temperature was also paid much attention.

In chapter 1, the usually used strengthening mechanisms for copper were summarized briefly. The problems in developing the Cu-Ti alloys with high electrical and strength were mentioned and the research status of several Cu-Ti-X alloys were introduced. The purpose of this research was summarized.

In chapter 2, the reaction behavior of Ti and C during the powder metallurgy process was investigated as the reinforced TiC particles are in-situ formed during the process. The samples preparation was through high-energy ball-milling followed by SPS and subsequent heat treatment. The SEM-EDX and TEM results revealed that the C plays a significant role in the reaction between Ti and C during this process and the TiC particle size is strongly depend on the C size. In addition, the transition of incomplete chemical reaction characterized by core-shell structure to complete reaction could be achieved by decreasing the C particle size. Finally, a schematic illustration showing the mechanism for high electrical conductivity and strength was proposed, as shown in Fig.1.

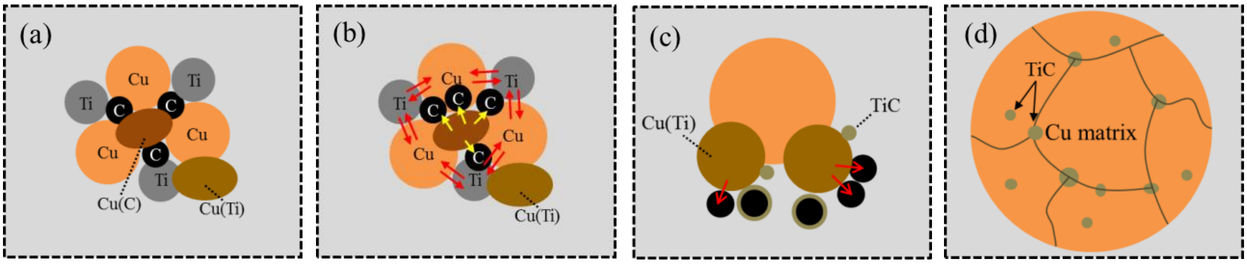

Fig.1 Reaction mechanism for high electrical conductivity and strength of Cu-Ti-C system: (a) fine-grained mixture of Cu-Ti-C after ball-milling; (b) interdiffusion betweent Cu and Ti, dissociation of the supersaturated solid solution Cu(C) during SPS; (c) Chemical reaction of Ti-C during SPS and heat treatment; (d) The idea final microstructure.

In chapter 3, according to the results of chapter 2, the TiC-strengthened copper alloys have been successfully produced by a self-developed two-step ball-milling (TSBM) process followed by SPS, heat treatment and subsequent hot press process. Firstly, the effects of ball-milling parameters on the electrical and mechanical properties of Cu-TiC alloys were analyzed. Nanoscale Ti-C mixture could be obtained during the 1^{ST} step using the TSBM process. The microstructure evolution and electrical conductivity variation indicated that residual Ti in copper matrix in SPS samples was ascribed to the incomplete transformation of Ti and C into TiC, while this transformation was accomplished in the following heat treatment process. The microstructural characterization revealed that nanoscale TiC particles were homogeneously dispersed in the copper matrix, while some TiC particles agglomerations could be observed. The TiC particles were found to mainly located in the grain boundaries by using TEM-EDS mapping analysis. The dissolved Ti in copper matrix was found to be the predominant factor lowering the electrical conductivity. The TiC particles formed during ball-milling process was found to be less effective in improving the strength than that in-situ formed during SPS and subsequent HT process. The effects of SPS and heat treatment conditions on the properties of Cu-TiC alloys were also investigated. The results of relative density, Vickers microhardness and electrical conductivity revealed that the optimized SPS temperature and pressure were 800 ℃ and 80 MPa respectively and the heat treatment conducted at 950 ℃ for 1~1.5 h has been confirmed to be the rational.

In chapter 4, the investigation on improved two-step ball-milling (ITSBM) process revealed that addition of a certain volume fraction of copper powders into 1^{ST} step could prevent the nanoscale particles agglomerations. The microstructural characterization showed that the ultrafine-grained (UFG) structure developed in SPS process could maintained thermostable through the whole process. The electrical conductivity and microhardness variation showed a similar characteristic with that of TSBM process. The UTS of the Cu-2.0Ti-0.5C alloys prepared by ITSBM process exhibited a mean UTS of 714 MPa and elongation to fracture of 6.6%. The electrical conductivity indicated an average value of around 70% IACS. Besides, the adding content of Cu into 1^{st} step could affect the milled powders, which in turn affect the properties of prepared alloys.

In chapter 5, firstly, the hot deformation behavior of developed Cu-TiC alloys was investigated by carrying out the hot compression tests. The true stress showed a positive relationship with strain rate, and no obvious work hardening occurred during the hot compression. Besides, the yield drop phenomenon was observed with increasing strain rate, which might be attributed to the rapid generation of mobile dislocations from grain boundary sources. Through the study of different reduction from 0% to 60%, it was found that there was no change in grain size distribution, while the particles distribution could be improved with increasing reduction. The KAM map characterization revealed that no increasing number of dislocation walls or subgrains with increased reduction, which implying that the grain boundary sliding or rotation should be the predominant deformation mechanism for the UFG structure of Cu-Ti-C alloys. With the constant strain rate of 0.01 s^{-1} and reduction of 60%, no obvious microstructure change was observed at deformation temperature range of 400 °C~600 °C, while there is obvious grain growth was observed at the temperature of 700 °C. Grain refinement was found with the increasing strain rate from 0.001 s^{-1} to 1.0 s^{-1} with fixed temperature of 500 °C and reduction of 60%. The difficulty in recrystallization for the present Cu-Ti-C alloys was ascribed to the pinning points provided by grain boundary junctions and dispersed nanoscale TiC particles.

The investigation on the thermostability of prepared Cu-Ti-C alloys revealed that the present alloy could maintain stable grain size and microhardness value with annealing temperature up to 930 °C, while there was a slight drop in thermostability characterized by decreasing microhardness and grain growth when the annealing temperature was close to the melting point (Fig.2). According to the microstructural characterization, the high thermostability of developed Cu-Ti-C alloys could be interpreted by pinning of grain boundaries by nanoscale TiC particles (Fig.3).

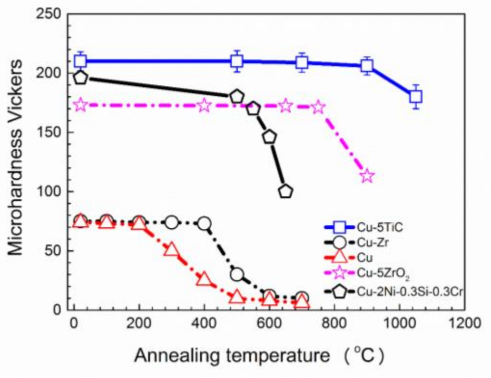

Fig.2 Microhardness variation with annealing temperature.

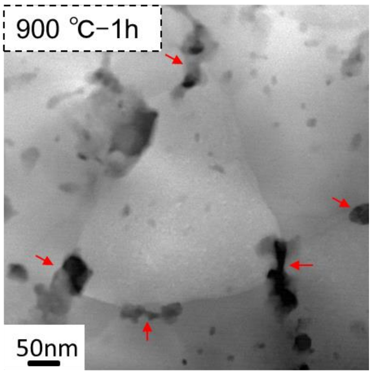

Fig.3 TEM-BF image showing pining effect of GBs by nanoscale TiC particles.

In chapter 6, the conclusions of this dissertation were summarized and the future work of this research was presented.