Materials Science Forum
ISSN: 1662-9752, Vols. 654-656, pp 1319-1322
doi:10.4028/www.scientific.net/MSF.654-656.1319

Online: 2010-06-30

Simultaneous Enhancement of Electrical Conductivities and Mechanical Properties in Cu-Ti Alloy by Hydrogenation Process

Atsunori Kamegawa[1, a], Toru Iwaki[1,2] and Masuo Okada[1,b]

[1]Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
[2]Graduate Student of Tohoku University (now at JFE Steel Corp.)

[a]kamegawa@material.tohoku.ac.jp, [b]okadamas@material.tohoku.ac.jp

Keywords: Cu-Ti alloy, hydrogenation, electrical conductivity, spinodal decomposition

Abstract. Effects of hydrogenation process of the microstructure, electrical conductivity and mechanical properties for the Cu-(1~3) mass%Ti alloys were investigated. During hydrogenation process at 350°C, 7.5 MPa for 48 h, the disproportionation reaction occurred with forming of Ti hydrides in the alloy. It is found that remarkable simultaneous improvements of mechanical strength of 1094 MPa and electrical properties of 21%IACS are obtained in the hydrogenated Cu-3mass%Ti alloy.

Introduction

Copper alloys have high electrical conductivity and good spring properties. So these alloys have been widely used for electrical wires, connectors or spring wires in Electrical and Electronic devices, such as PC, cell phone and so on. Especially, the Cu-Be-based alloys exhibit a high strength. However, the shortcomings of Cu-Be alloy are emitting of toxic gasses during production process and the high cost of Be. Recently, Cu-Ti alloys attract attentions with their high-strength as substitution of poisonous Cu-Be alloys. Although strength of Cu-Ti alloys is inferior to that of Cu-Be alloys, Cu-Ti alloys have other good properties, such as high spring property and abrasion resistance. In order to substitute Cu-Be alloys with Cu-Ti alloys, further enhancements of their mechanical properties such as ductility and strength are strongly required.

Cu-Ti alloys undergo spinodal transformation during aging [1] and the formation of fine-scale coherent/semicoherent D1a (Cu_4Ti) precipitates at high super-saturation causes high strength in Cu-Ti alloys [2-5]. In order to obtain higher strength of the alloy, other approaches are required. Among a number of investigations of the strength enhancement in Cu-Ti alloys, we have focused on using hydrogenation process for the alloys.

In our previous studies, Hydrogenation-Disproportionation-Desorption-Recombination (HDDR) process was performed for solid-solution alloys, such as Mg-based alloys (i.e. AZ91, AZ61, AZ31 and ZK60) [6-8], Al-Mg alloys [9] and Cu-Mg alloys [10]. It is reported HDDR process is effective for obtaining fine grains in these alloys.

Recently, we also reported the grain size refinements of Cu-3mass%Ti alloys by hydrogen heat-treatment of HDDR process [11]. The alloy is commercially available, and has been widely used for high-strength electrical conducting materials such as lead frames and connectors. During hydrogenation process, the disproportionation reaction occurred with forming of Ti hydrides in the alloy. With decomposition of Ti hydrides by the subsequent desorption process, Ti resolved into Cu matrix. In consequence, the original solid solution phase of the alloys formed. This means that the HDDR phenomena could take place in the Cu-3mass%Ti alloy. The grain size of the alloy is found to be about 20-50nm after HDDR treatments such as hydrogenation treatment at 350°C under hydrogen pressure of 7.5MPa for 48h, followed by the hydrogen desorption treatment at 530°C for 4h in vacuum. On the other hand, it is found that remarkable simultaneous improvements of mechanical strength and electrical properties are achieved in the hydrogenated alloy.

Semboshi *et al.* reported that the electrical conductivity of Cu-3at.%Ti alloy (Cu-2.3mass%Ti) is more than 65%IACS after aging at 500°C for 48h in hydrogen atmosphere[12-13]. This could be due to the reason that Ti content not only in the solid solution of Cu, but also in α-Cu_4Ti phase decreases effectively by aging in hydrogen atmosphere than that by aging in vacuum in forming Ti-hydrides. The hardness of the Cu-3at.%Ti alloy aged at 500°C for 1h in hydrogen atmosphere is the same as that aged in vacuum [14]. On the other hand, in the our previous study for Cu-3mass%Ti alloy, the nominal stress (1094MPa) of hydrogenated sample at 350°C is higher than that (908.8MPa) of aged sample in Ar-atmosphere.

Simultaneous improvements of electrical conductivity and mechanical strength in the present study will be due to lower temperature (350°C) of hydrogenation temperature and high hydrogen pressure of 7.5MPa, in comparing the studies of Semboshi *et al.,* although the composition of the studies alloy is slightly different. Further detailed studies are required to clarify the reason why these conditions yielded the excellent properties. This new finding that aging of the alloys in hydrogen gives the simultaneous improvements of electrical conductivity and mechanical strength, may be applicable to the other spinodal or precipitated- hardened alloys in the future

Dutkiewicz reported the existence of spinodal curve on the composition of about 2mass%Ti at 300-400°C [15] which temperature was reported as optimized hydrogenation process in Cu-3mass%Ti [11]. In the present investigation, we focused on the Ti content around spinodal composition in Cu alloy applying hydrogenation process. Then, the purpose of the present study is to investigate the effects of Ti content on the mechanical strength and electrical conductivity for the hydrogenated Cu-Ti binary alloys.

Experimental Procedures

The Cu-xmass% Ti alloys (x=1, 2, 3) were provided by Nippon Mining & Metals Co., Ltd. This sample was rolled after solution treatment and thickness of the sample is 50μm. Before the HDDR treatment, ultrasonic washing in acetone was carried out. Then, the hydrogenation of the samples was carried out at 350°C under a hydrogen pressure of 7.5MPa for 48h. The annealing under Ar atmosphere with same temperature and times was also performed for comparison with hydrogenation samples.

The crystal structure of alloys was characterized by X-ray diffraction. Microstructural observations were performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The hydrogen content of sample was measured by means of a fusion extraction analysis. The tensile tests were carried out by the samples with dimensions of 10mm x 3mm x 50μm utilizing SHIMAZU AUTOGRAPH AG-X universal testing machine with a crosshead speed of 25 mm/min. The electrical conductivity was measured by using the standard four-terminal methods at room temperature on samples with dimensions of cross-section were 1mm-2.5mm x 50μm and length of about 4-6mm.

Results and Discussion

Figure 1 shows stress-strain curves (S-S curves) of the Cu-x mass%Ti alloys (x=1, 2, 3) after hydrogenation at 350°C under a hydrogen pressure of 7.5MPa for 48h. Therefore, it can be said that Cu-Ti sample was hydrogenated during hydrogenation process. That means all samples could hydrogenate under the condition. In our previous work, it was found that the Cu-3mass% alloy decomposed to Cu-matrix phase, Ti-hydride ($TiH_{\sim 2}$) and D1a (Cu_4Ti) phase [11]. Figure 2 shows nominal stress of the corresponding alloys for as-rolled state, after hydrogenation or after annealing under Ar atmosphere at 350°C for 48h. It was found that he nominal stress of the alloys increased through the hydrogenation and the annealing. The nominal strengths of the alloy after hydrogenation and after annealing were almost same. On the other hands, the strength enhancements of the hydrogenated alloys were larger than that of the annealed alloys in the composition of more than 2mass%Ti. The nominal stress of the alloys increased with increasing Ti content. In order to measure the hydrogen content of the alloy, the fusion extraction analysis was conducted for some samples. All as-rolled and annealed alloys had less than 60ppm hydrogen. On the other hand, the hydrogen contents of the Cu- 1, 2, 3mass%Ti alloy were measured to be 123, 328, 871ppm, respectively. If Ti in Cu-3mass%Ti was fully -hydrogenated to TiH_2, the amount of hydrogen of Cu-3 mass%Ti could be estimated to be 0.09505mass%. Therefore, it can be said that Cu-3mass%Ti alloy was hydrogenated during hydrogenation process. However, the hydrogen contents of Cu-1, 2 mass%Ti alloys were comparatively little. Considering spinodal composition in Cu-Ti alloy around hydrogenation temperature, 350˚C, spinodal decomposition will proceed with the formation of Cu-rich and fine-scale D1a (Cu_4Ti) phase in hydrogenation process. During the decomposition, when hydrogen diffuses into alloys, Ti-hydrides formed in consumption of Ti in mainly D1a phase as well as some Ti content even in Cu-rich phase. It is speculated the fine Ti hydrides would be dispersed in spinodal decomposed phases.

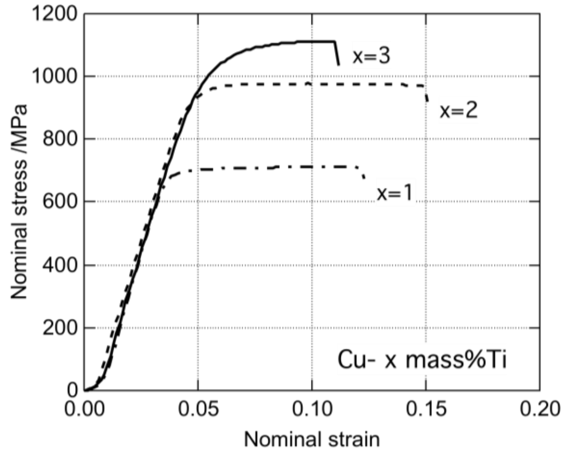

Fig. 1 stress-strain curves (S-S curves) of the Cu -x mass% Ti alloys after hydrogenation (x=1, 2, 3).

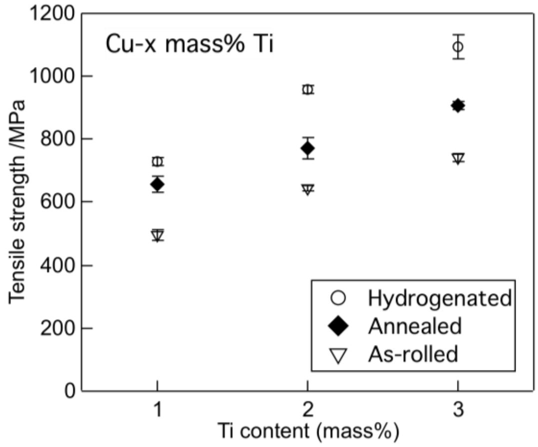

Fig. 2 tensile strength of the Cu -x mass% Ti alloys for as-rolled state, after hydrogenation or after annealing (x=1, 2, 3).

Figure 3 shows electrical conductivity of the alloys for as-rolled state, after hydrogenation or after annealing. The conductivity of the alloys increased with decreasing Ti content, because of decrease in the amount of Ti in Cu matrix. It was found that the electrical conductivity of the alloys increased through the hydrogenation and the annealing. Moreover, the increment conductivities of the hydrogenated alloys were larger than that of the annealed alloys.

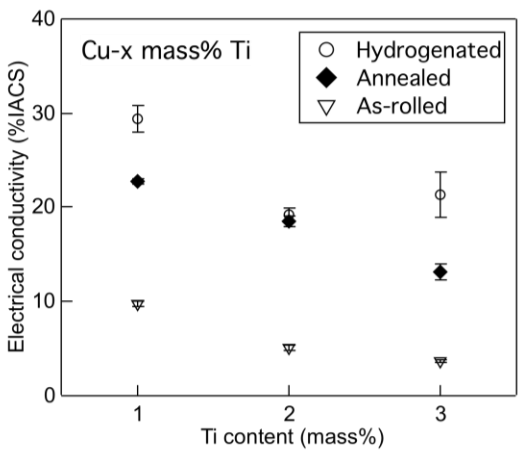

Fig. 3 electrical conductivity of the Cu -x mass% Ti alloys for as-rolled state, after hydrogenation or after annealing (x=1, 2, 3).

The reason why hydrogenated sample shows high conductivity seems to be interpreted as follows; The formation of Ti hydride and decrement of Ti content in Cu-rich phase cause increment of the conductivity. This could be understood in considering that the annealed sample shows 13.06%IACS where Cu-rich and D1a (Cu_4Ti) two phases will exist, judging from TEM observation of the alloy.

Summary

The effects of Ti content around spinodal composition on the mechanical strength and electrical conductivity for the hydrogenated Cu-Ti binary alloys were investigated. Simultaneous improvements of mechanical strength and electrical properties were obtained in the Cu-(1-3)mass% Ti alloys. Remarkable improvement of the strength was observed in the Cu-Ti alloys containing more than 2mass%Ti alloys. High mechanical strength of 1094MPa and high electrical conductivity of 21%IACS were obtained in the Cu-3mass%Ti alloy.

Acknowledgements

This study was partially supported by the Ministry of Education, Science, Sports and Culture, “Elements Science and Technology Project”. The authors extend the acknowledgements to Dr. Yuki and Mr. Etoh in Nippon Mining & Metals Co., Ltd for the discussions.

References

[1] J.L.Murray: Binary Alloys Phase Diagrams Second Edition (1990), 1494-1496.
[2] D.E. Laughlin, J.W. Cahn: Acta Metall., 23 (1975), 329-339.
[3] A.Datta and W.A.Soffa: Acta Metall.: 24 (1976) 987.
[4] S.Nagarjuna, M.Srinvivas, K.Balasubraman and D.S.Sarma: Mater. Sci. Eng.A 259 (1999) 34-42.
[5] W.A.Soffa, D.E. Laughlin: Prog. Mater. Sci., 49 (2004) 347-366.
[6] H.Takamura, T.Amemiya, A.Kamegawa, M.Okada: Mater. Trans. 41 (2000) 1142-1145.
[7] A. Kamegawa, T. Miyashita, H. Ogasawara, H. Takamura and M. Okada: Materials Science Forum, 419-422 (2003) 931-936.
[8] T. Miyazawa, Y. Kobayashi, A. Kamegawa, H. Takamura and M. Okada: Mater. Trans. 45 (2004) 384-387.
[9] A. Kamegawa, T. Funayama, J. Takahashi, H. Takamura and M. Okada: Mater. Trans. 46 (2005) 2449-2453.
[10] A. Kamegawa and M. Okada: TMS Proceedings of 137th Annual Meeting, (2008), 251-256.
[11] T. Iwaki, T. Kuriiwa, A. Kamegawa, H. Takamura1 and M. Okada: Mater. Trans. 50 (2009) 499-505.
[12] S. Semboshi and T .Konno: J. Mater. Res. 23 (2008) 473-477.
[13] S. Semboshi, T. Nishida, H. Numakura and T. Konno: Journal of the JRICu 47 (2008) 165-170. (In Japanese)
[14] S. Suzuki, K. Hirabayashi, H. Shibata, K. Mimura, M. Isshiki, and Y. Waseda: Scripta Mater. 48 (2003) 431-435.
[15] J. Dutkiewicz: Bull. Acad. Polon. Sci. 22 (1974) 323-328.