DEFECT INDUCED HARDENING AND TOUGHENING IN $Mn_3Cu_xGe_{1-x}N$ METALLIC PEROVSKITE

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Introduction

Anti-perovskite manganese nitride, Mn_3AN, where A is a metal or semiconductor element, is an intermetallic compound with a basic structure of fcc-Mn_3A crystal reinforced and stabilized by nitrogen insertion. These compounds show a variety of physical properties derived from the intimate relationship between magnetic properties and crystal lattice, these are magnetostriction, magnetoresistance, magnetocaloric effect, etc. Manganese copper nitride (Mn_3CuN) shows ferromagnetic transition at T_c=143K, which takes place without volume change. Recently, Takenaka had found out that by partial substitution of Cu sites to semiconductor element, Ge, the relaxer-like magnetovolume effect was restored, therefore, $Mn_3Cu_{0.5}Ge_{0.5}N$ ceramics showed negative thermal expansion (NTE) around room temperature [2]. Besides the giant NTE properties, Ge doping also provides high stiffness and hardness in Mn_3CuN ceramics [3]. Mn_3CuN based structural materials are attractive candidates for thermal expansion compensators for extremely stiff, stable, and lightweight zero thermal expansion composites.

In the present study, the authors propose another method to control the mechanical properties of Mn_3CuN families. Metallic perovskite, Mn_3AN is known to include large amount of nitrogen defects and they would modify its physical properties. The hardness and stiffness of the $Mn_3Cu_{1-x}Ge_xN$ ceramics are enhanced by the introduction of nitrogen defects and this effect is completely reversible. In $Mn_3Cu_{1-x}Ge_xN$ ceramics, hardening-softening (or brittle-ductile) transition is reversibly takes place by “breathing” nitrogen in atmosphere.

Experimental

$Mn_3Cu_{1-x}Ge_xN$ ceramics were obtained by a conventional powder metalogical method using Mn_2N, Cu, Mn and Ge powders. Details were described in the previous report [2]. Nitrogen defect concentration in $Mn_3Cu_{1-x}Ge_xN$ was controlled by annealing under the given nitrogen pressure and temperature conditions. For making a $Mn_3Cu_{1-x}Ge_xN$ with stoiciometric composition, sintering at 1073K at the nitrogen pressure of 6-8atm was required. Higher temperature sintering in vacuum (10^{-3}Pa) was appropriate for preparing nitrogen deficient $Mn_3Cu_{1-x}Ge_xN$ ceramics ($Mn_3Cu_{1-x}Ge_xN_{1-\delta}$). Sintering over 1173K under high vacuum condition (10^{-3}Pa) provides the specimen with 20% nitrogen deficient.

For the evaluation of the mechanical properties, the sintered specimens were cut into rectangular sheets with a dimension of 4.5x1x14 mm and finished to 1μm of roughness using electro-fused alumina abrasive.

Young's modulus, E, was determined by the flexure (σ)-load (P) relation obtained by the statistic bending test. Vickers hardness (Hv) test was conducted with the indentation load of P= 49N using a micro-Vickers hardness tester.

Result and Discussion

Stoichiometric Mn_3CuN ceramics are ductile materials with the Young’s modulus of 72-98MPa and Vickers hardness of 150-190Hv. The mother material for NTE material, Mn_3CuN is rather “soft” materials whose stiffness is far lower than that of traditional zero thermal expansion materials, Invar alloys. Here, we found out that its mechanical properties are modified by the nitrogen deficiency. Figure 1 (A) shows the Vickers indentation trace of nitrogen deficient $Mn_3CuN_{1-\delta}$ ceramics prepared from the stoichiometric mixture of Mn_2N, Mn and Cu under high vacuum (10^{-3}Pa). The Mn_3CuN ceramics had conventionally been synthesized in high pressure (6-8 atm) N_2 atmosphere to avoid the production of nitrogen defects. We did synthesize the $Mn_3Cu_{1-x}Ge_xN$ ceramics in vacuum in order to introduce the nitrogen defects on purpose. The nitrogen deficiency δ in $Mn_3CuN_{1-\delta}$ is checked in advance and δ is evaluated to be about 0.2 in the specimen sintered at 1123K. Vickers hardness calculated from the dimension of the indentation trace is enhanced to 360-400Hv, while those of stoichiometric Mn_3CuN sintered at 1073*K* is 170Hv in average. In Figure 1(A), median cracks are not extended from the corner of the indentation trace and this result indicate that the $Mn_3CuN_{1-\delta}$ remains ductile, despite it is hardened due to the introduction of nitrogen defects. Effect of diverse atoms (Ge) on the indentation by Vickers test is demonstrated in Figure 1(B). The hardness is enhanced to be 590-600Hv by 50% of Ge doping. Simultaneously, ductility disappeared and the original ductile properties became brittle properties.

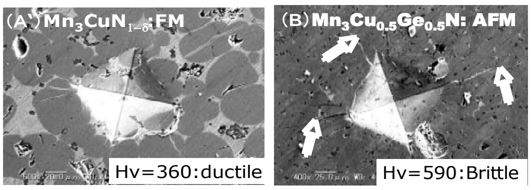

Figure 1: Top view of the Vickers indentation trace of (A) $Mn_3CuN_{1-\delta}$ and (B) $Mn_3Cu_{0.5}Ge_{0.5}N$ ceramics. Radial cracks observed in $Mn_3Cu_{0.5}Ge_{0.5}N$ are marked with white arrows.

Physical properties including mechanical properties of a series of Mn_3AN compounds are possibly modified by the introduction of both diverse atoms and nitrogen defects. The relationship between Ge content, x, and Vickers hardness of the $Mn_3Cu_{1-x}Ge_xN$ ceramics with and without nitrogen defects is summarized in Figure 2. The hardness of stoichiometric $Mn_3Cu_{1-x}Ge_xN$ gradually increases with an increase in Ge content. Young's modulus of $Mn_3Cu_{0.5}Ge_{0.5}N$ sintered body is evaluated to be 220.6-318.8GP and this value go well beyond the standard of the conventional low thermal expansion materials; in other words, higher stiffness and larger NTE properties are achieved by Ge doping of Mn_3CuN metallic perovskite. By the introduction of nitrogen defects, the hardness and stiffness are additionally enhanced in all the composition (0<x<0.5). The enhancement in hardness is remarkable in lower Ge content specimens.

It had already reported that high concentration of nitrogen defects dramatically modified the magnetic and related thermal expansion properties of $Mn_3Cu_{1-x}A_xN$ ceramics [4]. The effect of nitrogen defect introduction on the thermal expansion properties of Sn doped Mn_3CuN ceramics had been discussed by Takenaka and NTE properties of $Mn_3Cu_{0.5}Sn_{0.5}N$ are changed to be zero thermal expansion by the introduction of 20% of nitrogen defects [5]. In the present $Mn_3Cu_{1-x}Ge_xN$ series, the nearly zero thermal expansion observed in nitrogen deficient $Mn_3Cu_{0.5}Ge_{0.5}N_{1-\delta}$.

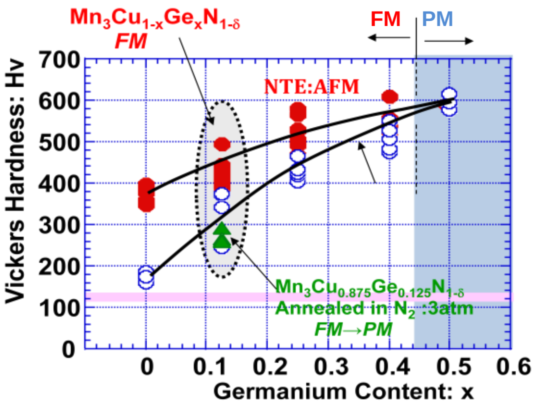

Figure 2: Vickers hardness: Hv as a function of germanium content: x of $Mn_3Cu_{1-x}Ge_xN$ (PM: Paramagnetic Metal) and $Mn_3Cu_{1-x}Ge_xN_{1-\delta}$ FM:Ferromagnetic Metal). At x=0.5, both $Mn_3Cu_{1-x}Ge_xN$ and $Mn_3Cu_{1-x}Ge_xN_{1-\delta}$ specimens are PM at room temperature.

Figure 3 shows the effect of nitrogen deficiency on the magnetic susceptibility of $Mn_3Cu_{0.875}Ge_{0.125}N$ ceramics. Magnetic ordering structure of $Mn_3Cu_{0.875}Ge_{0.125}N$ is ferromagnetic and its Currie temperature: T_c is judged to be 135K. However, when the specimen with the same composition was prepared in vacuum (10^{-3}Pa), its T_c moved to 330K and the specimen showed ferromagnetic properties even at room temperature. The nitrogen defect induced room temperature ferromagnetism had reported by Takenaka in Mn_3CuN, which is characterized by second-order like FM-PM transition (Tc=390K) remaining its cubic crystal structure[4]. The crystal lattice of nitrogen deficient $Mn_3Cu_{0.875}Ge_{0.125}N_{1-\delta}$ remains cubic at room temperature and the mechanism of this defect induced ferromagnetism in $Mn_3Cu_{0.875}Ge_{0.125}N$ would be similar to that reported by Takenaka.

As is shown in Figure 2, the Vickers hardness of nitrogen deficient $Mn_3Cu_{0.875}Ge_{0.125}N$ is 390-500Hv, which is about 30% enhanced by the introduction nitrogen defects. Young's modulus of this specimen is also enhanced to 160-210GPa.

By annealing the nitrogen deficient specimen, $Mn_3Cu_{0.875}Ge_{0.125}N_{1-\delta}$ in high-pressure nitrogen gas, its ferromagnetic property (T_c=330K) is disappeared and it shows paramagnetic property at 300K as is shown in Figure3. Accompanied by the ferromagnetic to paramagnetic transition triggered by high pressure N_2 annealing, the mechanical properties of $Mn_3Cu_{0.875}Ge_{0.125}N_{1-\delta}$ changed dramatically. "Hardened" specimen (Hv=423) due to the extraction of nitrogen can be switched back to "soft"(Hv=330) by the re-insertion of nitrogen. The Vickers hardness of the $Mn_3Cu_{0.875}Ge_{0.125}N_{1-\delta}$ ceramics after annealing in high-pressure N_2 (3.1atm) at 1033K is over-plotted in Figure 2 (Indicated by green triangle). "Hardened" $Mn_3Cu_{0.875}Ge_{0.125}N_{1-\delta}$ turned to be "soft" and simultaneously, its ferromagnetic property disappeared.

In the system $Mn_3Cu_{1-x}Ge_xN_{1-\delta}$, reversible tuning in magnetic and mechanical properties is possible by controlling the nitrogen defect concentration, δ. $Mn_3Cu_{1-x}Ge_xN$ based structural materials will have a characteristic feature of "variable" hardness and stiffness tuned by the atmosphere (nitrogen pressure) during annealing process. Accordingly, reversible tuning in thermal expansion properties will also be possible in this system.

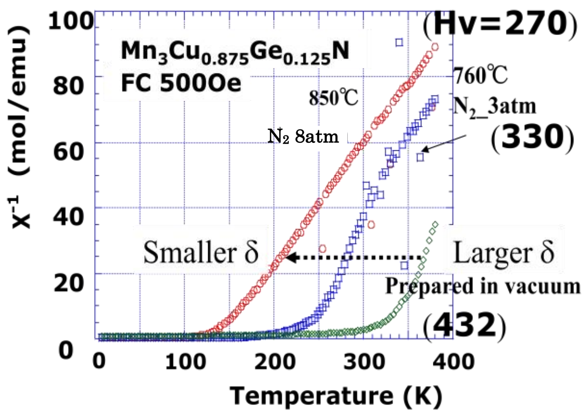

Figure 3: Inverse magnetic susceptibility of $Mn_3Cu_{0.875}Ge_{0.125}N$ and $Mn_3Cu_{0.875}Ge_{0.125}N_{1-\delta}$. By annealing in high-pressure N_2, ferromagnetic, $Mn_3Cu_{0.875}Ge_{0.125}N_{1-d}$ shows paramagnetic, while $Mn_3Cu_{0.875}Ge_{0.125}N_{1-\delta}$ is ferromagnetic at room temperature.

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