Abnormal Grain Growth Induced by Cyclic Heat Treatment

Toshihiro Omori,1* Tomoe Kusama,1 Shingo Kawata,1 Ikuo Ohnuma,1 Yuji Sutou,1 Yoshikazu Araki,2 Kiyohito Ishida,3 Ryosuke Kainuma3

Received 3 June 2013; accepted 22 July 2013; published 27 September 2013

In polycrystalline materials, grain growth occurs at elevated temperatures to reduce the total area of grain boundaries with high energy. The grain growth rate usually slows down with annealing time, making it hard to obtain grains larger than a millimeter in size. We report a crystal growth method that employs only a cyclic heat treatment to obtain a single crystal of more than several centimeters in a copper-based shape-memory alloy. This abnormal grain growth phenomenon results from the formation of a subgrain structure introduced through phase transformation. These findings provide a method of fabricating a single-crystal or large-grain structure important for shape-memory properties, magnetic properties, and creep properties, among others.

Most metals and ceramics have a polycrystalline structure that is composed of single-crystalline grains separated by interfaces, called grain boundaries (GBs). There are multiple types of GBs—including low-angle, high-angle, and coincidence—that each posses a partial randomness in the position of the atoms and are of higher energy than the neighboring crystal. Therefore, the polycrystalline structure is thermodynamically unstable, and the average grain size can increase during heat treatment to reduce the total GB area. The increase of average grain size occurs due to a gradual growth of the larger grains and elimination of the smaller ones, through GB migration. In certain circumstances, selective growth of a few grains occurs by engulfing the neighboring ones, resulting in formation of considerably huge grains; this phenomenon is known as abnormal grain growth (AGG). AGG is used in the fabrication process for Fe-Si electrical steels that have excellent magnetic properties with small core loss and are used in electrical power transformers, motors, and generators. In this alloy, the texture of Goss orientation ([110]<001>) showing higher magnetic property is realized by AGG (f) induced by second-phase (inhibitor) dispersion and thermomechanical treatment (2).

Although the mechanism for AGG has not fully been understood, it has been reported that strong retardation of normal grain growth (3–5) is one of the important factors (2).

A well-known technique to obtain AGG is the strain-annal method, consisting of a small macroscopic deformation followed by thermal annealing (6). AGG is brought about by encroaching subgrain structure, which is formed by rearrangement of dislocations introduced by the macroscopic deformation. It has also been demonstrated that a single crystal can be obtained in a wire and plate by straining and subsequent annealing with a temperature gradient (7–9). Another technique to produce a large grain or a single crystal in the solid state is the dynamic AGG, consisting of plastic straining at elevated temperatures (10). These methods are only applicable to samples with a simple shape, such as a sheet or wire, in which fracture does not occur by slight plastic deformation.

We have determined a simpler method to obtain AGG by cyclic heat treatment without macroscopic deformation in Cu-Al-Mn shape-memory alloys (SMAs). Cu-Al-Mn (17 atomic % Al) alloys quenched from the β (body-centered cubic) single-phase region at high temperatures exhibit shape-memory properties associated with the martensitic phase transformation (%).

According to the Cu-Al-Mn (10 atomic % Mn) phase diagram (fig. S1), because the Cu-Al-Mn (17 atomic % Al) alloy has the α (face-centered cubic) + β two-phase structure in the temperature region below ~650°C, the precipitation of the α phase occurs during cooling from the β-phase region or isothermal aging at lower temperatures. AGG of the β phase was realized by a process (Fig. 1) of slow cooling from the β-phase region (e.g., 900°C) to the α + β two-phase region (e.g., 500°C) and subsequent heating to the β single-phase region (e.g., 800°C), as shown in Fig. 2B. Figure 2C shows the microstructure of a Cu11.6Al17Mn11.4 alloy sheet obtained by the cyclic heat treatment illustrated in Fig. 1. Abnormally large grains with lengths from 5 to 22 mm are formed. In contrast, in an isothermally annealed sheet, the maximum grain diameter of the β phase is ~2 mm, as shown in Fig. 2A. Although the final annealing at 900°C was performed for a full 24 hours. Furthermore, AGG occurred by multiple cyclic heat treatments, in contrast to the conventional AGG where the growth rate of abnormal grains drastically decreases with increasing mean grain size. Figure 2D shows the microstructure of the sheet specimen after five cyclic heat treatments. A grain approaching 50 mm in length was obtained with a total treatment time of 20 hours.

To understand the origin of the AGG, we used the electron backscatter diffraction (EBSD) technique to analyze the microstructure in the initial stage of the grain growth. In Figure 3, panels A and B, respectively, show the quasicolored orientation mapping of the β phase and the grain reference orientation deviation indicating the deviation from the average orientation of the grain for Cu11.6Al17Mn11.4 quenched from 730°C, which is just above the α solvus temperature (726°C). Surprisingly, small subgrains with a mean diameter of ~100 μm, possessing orientation deviations from 1° to 2° to one another, are observed in every preexisting grain. A similar subgrain structure is formed by recovery through deformation and low-temperature annealing. The subgrains, however, are consumed by recrystallization through further high-temperature annealing. Thus, the fully recrystallized specimen contains only a low density of dislocations and subboundaries in the recrystallized grains. In the present case, because the specimens were initially annealed at a high enough temperature to complete the recrystallization process, this subgrain structure is not attributed to the strain annealing. No subgrain structure was observed after water quenching from the β single-phase region without cyclic heat treatment, meaning that the subgrains were not produced during water quenching but were preserved from the high-temperature state. The formation of such a subgrain structure occurs in the precipitation and dissolution of the α phase during the cyclic heat treatment after recrystallization. Although the mechanism responsible for the AGG has not yet been determined, the formation of the subgrain structure is strongly related to this phenomenon. For example, the subgrain-boundary energy might be one of the driving forces.

To clarify the formation mechanism of the subgrain structure, we used EBSD to examine the two-phase microstructure after precipitation of the α phase. Figure 4A shows the quasicolored orientation mapping of the β phase (top) and α phase (middle) and grain reference orientation deviation mapping of the β phase (bottom) in a Cu-Al-Mn alloy slowly cooled from 900°C to 500°C. In the grain reference orientation deviation map, the orientation gradients up to 3° and, occasionally, 5° are visible in the β phase around the α precipitates. Figure 4B shows the...
Fig. 2. The microstructure of a Cu-Al-Mn alloy with simple iso-
thermal heat treatment and cyclic heat treatment. (A) The microstructure of 
(a) Cu71.6Al17Mn11.4 alloy sheet annealed at 900°C for 24 hours. (B) The 
microstructure of a Cu-Al-Mn alloy sheet heated to 500°C. (C) The 
microstructure of a Cu71.6Al17Mn11.4 alloy sheet annealed at 900°C for 5 min, 
followed by cooling to 500°C and, subsequently, heating to 800°C with 
a holding time of 10 min. One grain abnormally grows to ~7 mm. (D) The 
microstructure of a Cu71.6Al17Mn11.4 alloy sheet subjected to five cycles of the above-mentioned 
heat treatment, showing grains with sizes on the centimeter scale.

Fig. 3. Crystallographic orientation of a Cu-Al-Mn sheet heated to 
730°C and then quenched. (A) Quasi-colored orientation mapping 
(OM) of a Cu-Al-Mn alloy sheet quenched from 730°C in the heating 
process after cooling from 600°C to 500°C. The EBSD technique was used to 
analyze the microstructure. The colors correspond to crystal direction 
parallel to the normal direction given in the stereographic triangle. (B) 
Grain reference orientation deviation (GROD) mapping, where the color 
value of every pixel is calculated as the misorientation angle of this pixel 
with respect to a reference orientation (average orientation of a grain) 
in the same grain. Subgrains are shown in every normal grain. Arrows indicate 
the migration of GBs.

Fig. 4. Microstructure and crystallo-
graphic orientation in the α and β two-
phase of a Cu-Al-Mn alloy cooled from 
900°C. (A) Quasi-colored OM of the β 
phase (top) and the α phase (middle) in nor-
mal direction and GROD mapping of the β 
phase (bottom) of Cu-Al-Mn quenched from 
500°C. (B) (110) pole figure of the β phase 
(top) and α phase (bottom) of Cu-Al-Mn quenched from 500°C. RD, rolling direction; 
TD, transverse direction. (C) Quasi-colored OM of the α and β phases (left) in normal 
direction and GROD mapping of the β phase (right) of a Cu-Al-Mn alloy quenched from 
680°C, showing the formation of a subgrain structure in the matrix phase. The 
color key for OMs is given in the stere-
ographic triangle of Fig. 3A.
Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide

Maria R. Lukatskaya,1,2 Olha Mashtalir,1,2,4 Chang E. Ren,1,2,4 Yohan Dall’Agne,1,2,3,4 Patrick Rozier,1 Pierre Louis Taberna,1 Michael Naguib,2,2 Patrice Simon,1,4 Michel W. Barsoum,3 Yuri Gogotsi1,2,†

The intercalation of ions into layered compounds has long been exploited in energy storage devices such as batteries and electrochemical capacitors. However, few host materials are known for ions much larger than lithium. We demonstrate the spontaneous intercalation of cations from aqueous salt solutions between two-dimensional (2D) Ti₃C₂ MXene layers. MXenes combine 2D conductive carbide layers with a hydrophilic, primarily hydroxyl-terminated surface. A variety of cations, including Na⁺, K⁺, NH₄⁺, Mg⁺, and Al³⁺, can also be intercalated electrochemically, offering capacitance in excess of 300 farads per cubic centimeter (much higher than that of porous carbons). This study provides a basis for exploring a large family of 2D carbides and carbonitrides in electrochemical energy storage applications using single- and multivalent ions. With the increased demand for portable and clean energy, electrochemical capacitors have been attracting attention because of their much greater power density and cyclability relative to Li batteries (1, 2). However, electrical double-layer capacitors (EDLCs), in which the capacity is due to the electroosorption of ions on porous carbon electrodes, have limited energy density (2). Pseudo-capacitors, in which the capacity is due to redox reactions, provide higher energy densities but usually suffer from shorter cyclic lifetimes. RuO₂ nanosheets have been used in redox capacitors and have shown impressive capacitance and cyclability, but they are quite expensive to produce (2, 3). Energy density enhancement of capacitors can be achieved by using hybrid devices, which combine a battery-like redox electrode and a porous carbon electrode (4). Another approach is to use materials in which charge storage is due to intercalation of ions between atomic layers because the capacitances—even at high discharge rates—are high. For example, nanocrystalline Nb₂O₅ films with storage capacities of ~130 mAh g⁻¹ at rates as high as 10 C (charge/discharge in 6 min) for Li⁺ ions in organic electrolytes have been reported. The specific structure of this material can best be described as a crystalline network with two-dimensional (2D) transport paths for ions between atomic layers; thus, even thick electrodes show excellent behavior (5). Another example is Mg-buserite electrodes, which exhibit good Na⁺ ion intercalation capacitances but have poor electrical conductivities (6). Most materials for electrodes that can provide intercalation or surface redox capacitances are poor electronic conductors such as graphene oxide or TiO₂ (7) or are hydrophobic (e.g., graphene (8)).

Recently, we reported on a large family of 2D materials that we labeled “MXenes,” which combine good electrical conductivities with hydrophilic surfaces. MXenes are 2D materials synthesized by the extraction of the “A” layers from the layered carbides or carbonitrides known as MAX phases. The latter have a general formula of M₁+xAXₙ (n = 1, 2, 3), where M represents a transition metal; A usually represents a III A or IV A element (such as Al, Ga, Si, or Ge); and X represents C and/or N (9). The MXenes Ti₃C₂ (10), Ti₃C, Ti₃C₂, TiNB, and (V₀.₅C₀.₅)ₙC₃(Ⅱ) (11), have been fabricated by immersing Al-containing MAX powders in HF solution at room or slightly

References and Notes

Acknowledgments: This work was supported by the Japan Science and Technology Agency and by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science and a Grant for Excellent Graduate Schools from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank K. R. A. Ziebeck, Cavendish Laboratory, University of Cambridge, for his help in critical reading of the manuscript. T.-O. T., R.K., K.I., T. Tanaka, S. Kise, K. Nakazato, K. Ishikawa, M. Nakano, and S. Teshigara are inventors on Japanese patent application number 2013-099996, applied for by Tohoku University, Furukawa Techno Material Co., and Furukawa Electric Co.

Supplementary Materials
www.sciencemag.org/content/341/6153/1500/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S3
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19 March 2013; accepted 1 August 2013 10.1126/science.1238017