Invar-type Effect induced by Cold-rolling Deformation in Shape Memory Alloys

著者	大森 俊洋
journal or publication title	Applied Physics Letters
volume	80
number	23
page range	4348-4350
year	2002
URL	http://hdl.handle.net/10097/34871

Invar-type effect induced by cold-rolling deformation in shape memory alloys

R. Kainuma,[a)] J. J. Wang, T. Omori, Y. Sutou, and K. Ishida
Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan

(Received 17 December 2001; accepted for publication 15 April 2002)

Since the discovery of Fe–Ni alloys showing low thermal expansion (LTE) in 1896, many Invar alloys have been developed based on magnetovolume effect where negative thermal expansion is induced by magnetic transformation. Herein, we show that the control of stress-induced martensitic transformation due to cold working of the Cu–Zn–Al polycrystalline alloy results in the LTE. This type of LTE material is easily fabricated by conventional cold rolling, and the coefficient of thermal expansion in the range from about 0 to 32×10^{-6} K^{-1} can be obtained by controlling the reduction ratio. The LTE effect due to the present method can also be obtained for other shape memory (SM) alloys such as Ni–Ti, Cu–Mn–Al and Ni–Al base alloys, which have high potential for various practical applications. [DOI: 10.1063/1.1485118]

It is well known that thermal expansion is one of the intrinsic properties of a material which is very difficult to control. In 1896, an exceptionally low thermal expansion (LTE) named the Invar effect was found in Fe–Ni binary alloys.[1,2] The Invar effect is related to the magnetovolume effect where negative thermal expansion (NTE) is induced by magnetic transition from the paramagnetic to the ferromagnetic or anti-ferromagnetic phase, and the coefficient of thermal expansion (CTE) is given as the total value of the normal and the negative thermal expansion terms.[2,3] Invar alloys have been extensively investigated and many kinds of Invar alloys have been developed in the 20th century.[2–5]

Materials with a low CTE are required in the various fields, particularly, in electronic packaging technology, because the thermal stress generated by the difference of the CTE between silicon, ceramics, polymer, etc., in the electronic devices strongly affects the mechanical or electrical properties in the packaging.[6,7] Fe–Ni Invar alloys are widely used in this field, although they have a low electric conductivity. On the other hand, while having a high electronic conductivity, Cu-base alloys show a high CTE (about 17 $\times10^{-6}$ K^{-1}) and no Invar-type of Cu alloy has been developed because no magnetic transformation appears. As mentioned above, the LTE in the Invar alloys is due to second order magnetic transition where the volume change is a function of the degree of the long-range order of spins. This type of transition shows the following two important features required for the LTE effect: (1) this transition maintains the reversibility of thermal expansion in the low temperature region where atomic diffusion is restricted, and (2) the temperature interval in which the LTE appears ranges over several hundred Kelvin. The present study shows that thermoelastic martensite (TM) transformation is applicable for obtaining LTE. In the TM transformation, the shape memory strain under a fixed stress is reversible for the cyclic temperature change, indicating that the above requirement of (1) holds, while the transformation occurs only in a very small temperature interval within a couple of decades Kelvin, which does not satisfy the second requirement.[7] Herein, we show that cold rolling of the Cu-base TM alloys results in the stress-induced (SI) martensite transformation at high temperatures over the martensitic transformation starting temperature (Ms) and widens the transformation temperature interval over one hundred Kelvin.

Cu–21.6 at. % Zn–10.2 at. % Al alloy ingots 20 mm in diameter and 100 mm in height were prepared by induction melting of pure Cu(99.9%), Zn(99.9%) and Al(99.9%) in an argon atmosphere. The obtained ingots were hot rolled up to about 4 mm in thickness at 800 °C, and then cut into small pieces and heat treated at 650 °C for 15 min, followed by aging treatment at 150 °C for 15 min to stabilize the Ms temperature. The sheet specimens were carefully ground to obtain clear, parallel surfaces. After measurement of thickness, the specimens were cold rolled in the direction parallel to the direction of hot rolling up to various reduction rates at room temperature. After the cold rolling at about 25 °C, the specimens were cut into cubes, and thermal expansion was measured by dilatometer (DL). The DL measurement was started at 90 °C and performed in the interval between −100 and 90 °C. In order to examine the characteristic features of texture before and after cold rolling, the three sections normal to the rolling direction RD, the transverse direction TD and the normal direction ND were cut from the specimens, and each surface was analyzed by x-ray diffraction (XRD) techniques using Cu $K\alpha$ radiation at room temperature. The martensitic transformation temperatures of the deformation-free specimen determined with DL were Ms=−23 °C, transformation finishing temperature: $Mf=-42$ °C, reverse transformation starting temperature: As=−22 °C and finishing temperature: $Af=-8$ °C.

Figure 1(a) shows thermal expansion curves in the RD obtained from the as-cold-rolled specimens in comparison with those from pure Cu and Fe–40.5 Ni Invar alloy.[8] It can be seen that the shrinkage of specimen during heating, i.e., negative thermal expansion (NTE), due to reverse transformation is enhanced by the cold rolling in the low reduction

[a)]Electronic mail: kainuma@material.tohoku.ac.jp

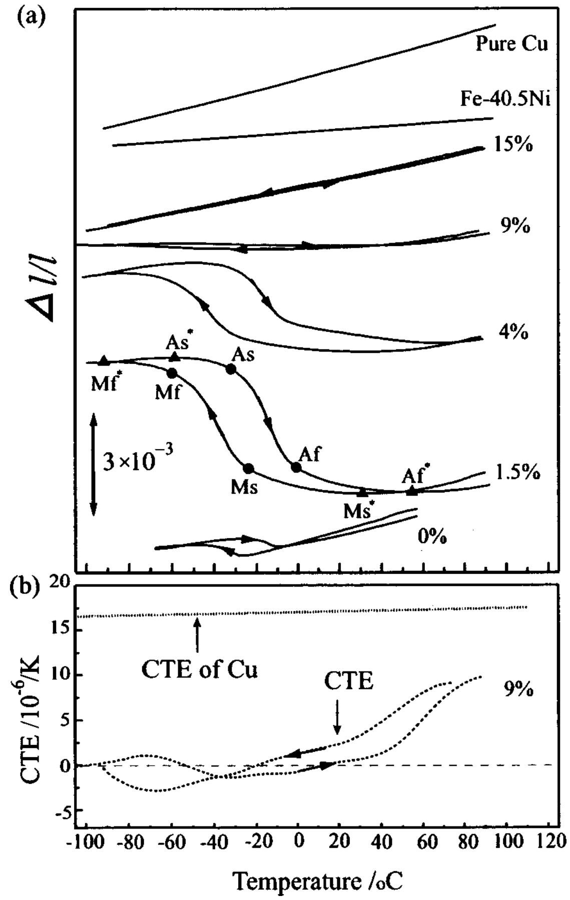

FIG. 1. (a) Thermal expansion curves in the rolling direction of the as-cold-rolled specimens. The reduction rate from the initial thickness is indicated by a percentage on every curve. (b) Temperature dependence of CTE values of 9% specimen. It should be noted that the LTE within CTE$\approx 0\pm 3\times 10^{-6}$ ranges from -100 to about 40 °C.

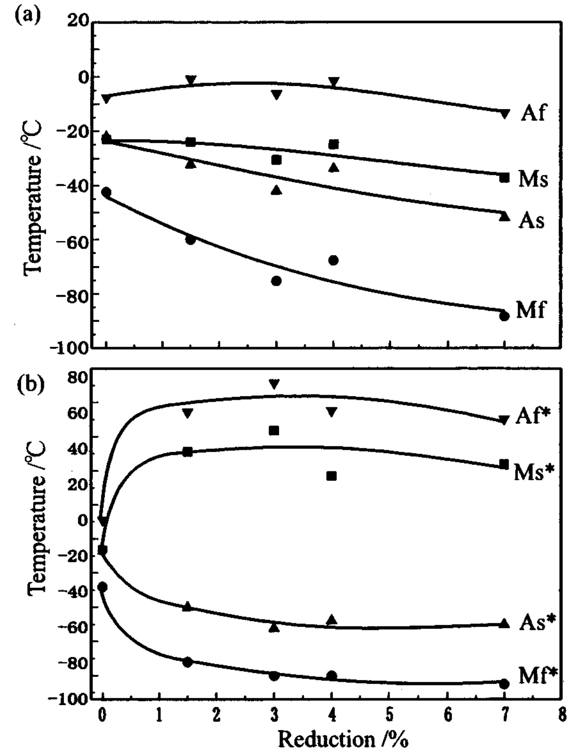

FIG. 2. Martensitic transformation temperatures of the specimens before and after cold rolling defined by the temperatures with (a) minimum curvature and (b) CTE$=0$ as demonstrated in Fig. 1.

region, while high reduction over several percent results in decrease of the transformation shrinkage. It should be noted that a curve within CTE$\approx 0\pm 3\times 10^{-6}$ at the temperatures ranging from -100 to about 40 °C can be obtained in the specimen cold rolled up to 9% reduction as plotted in Fig. 1(b). On the basis of these data obtained by DL measurement, two series of transformation temperatures were determined as plotted in Figs. 2(a) and 2(b), respectively, where Ms, Mf, As and Af in Fig. 2(a) are defined as temperatures which show minimum curvature in the cooling and heating curves, and Ms*, Mf*, As* and Af* in Fig. 2(b) are as those with CTE$=0$, as demonstrated in the DL curves obtained from the specimen cold rolled to 1.5% reduction in Fig. 1. It is shown in Fig. 2(a) that while the Ms and Af temperatures and the hysteresis intervals (i.e., Af-Ms and As-Mf) only slightly change, the transformation temperature intervals (i.e., Ms-Mf and Af-As) increase with increasing reduction rate. This result is similar to that obtained by tensile deformation in the NiTi alloys, as previously reported.[9,10] On the other hand, it is shown in Fig. 2(b) that (1) the Ms* and Af* increase and the Mf* and As* decrease drastically even with a very low degree of deformation, (2) both the temperature intervals, Ms*-Mf* and Af*-As*, reach at about 130 °C at 1.5% reduction and remain relatively constant against further deformation, and (3) the hysteresis intervals Af*-Ms* and As*-Mf* are comparable to Af-Ms and As-Mf, respectively. Recently, Lu and Weng[11] developed a micromechanical theory for the thermally induced phase transformation under the applied stress in the shape memory alloys. According to their theory, the thermal hysteresis loop during cooling and heating under an applied stress shifts horizontally to the high temperature direction as the level of applied stress increases. Since the pre-deformation by the cold rolling may bring about a distribution of a lot of levels of the internal stress in the specimen, the transformation temperature interval may be widened. Furthermore, the present results suggest that internal stress fields cause not only SI transformation in the high temperature region over Ms*, but also stabilize the austenite phase in the low temperature region under Mf* during cooling. It can be seen from Fig. 1 that the NTE due to the thermal transformation denoted by Ms to Af decreases and that the contribution of the SI transformation to the NTE becomes dominant with increasing reduction rate. This result means that the internal residual stress increases and becomes more homogeneous with increasing reduction rate.

One of the most interesting characteristic features in this LTE material is an anisotropy of the TE properties as shown in Fig. 3(a). The CTE in the RD is roughly zero in the temperature range below 60 °C, while those in the TD and ND are positive all over the temperature region examined. It is interesting to note that the average value of CTE of all the directions RD$=0.5\times 10^{-6}$, TD$=13\times 10^{-6}$ and ND$=32\times 10^{-6}$ K^{-1} at room temperature is about 15×10^{-6} K^{-1}, near the CTE of the Cu-base alloys. This result suggests that this phenomenon is essentially caused by the anisotropy of displacement due to SI martensitic transformation. In order to examine the origin of the anisotropy of thermal expansion in different directions after cold rolling, XRD on the RD, TD

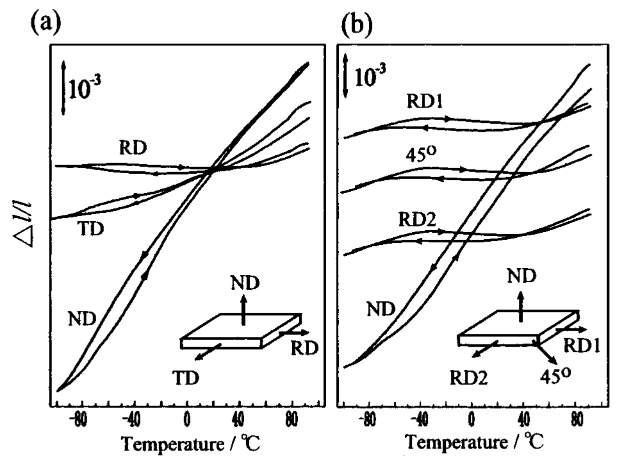

FIG. 3. The anisotropy of thermal expansion obtained from the specimen cold rolled to 9% reduction. (a) One directional rolling and (b) cross rolling alternately to RD_1, RD_2 and 45° between the RD_1 and RD_2.

and ND sections was performed. Figure 4(a) shows the result of XRD of the three sections at room temperature after 6% reduction. It can be seen that, whereas most reflections are from the 6M (9R)-type martensite phase, the peak intensity of $(006)_{6M}$ in the TD section is much stronger than those in the RD section and the ND section, and that of the $(020)_{6M}$ in the ND section and the $(200)_{6M}$ in the RD section are relatively strong. These results mean that the martensite phase induced by cold rolling has a crystallographic anisotropy where the $(006)_{6M}$, $(020)_{6M}$ and $(200)_{6M}$ are roughly parallel to the TD, ND and RD sections, respectively, as demonstrated in Fig. 4(b). According to the lattice correspondence between the B2 parent and 6M martensite phases,[12] the lattice distances of the $[100]_{6M}$, $[001]_{6M}$ and $[010]_{6M}$ directions parallel to the RD, TD and ND increase by about 7.8%, 3.8% and -8.9%, respectively, due to the martensitic transformation during cooling. It is apparent from this relation that the some martensite variants most suitable to release the applied stress as illustrated in Fig. 4(c) are preferentially induced during cold rolling and stabilized in the high temperature region over the Af temperature. This phenomenon can be explained as a kind of two-way shape memory effect.[7] It is emphasized that the Inver effect due to the present method can also be obtained for other SM alloys such as Ni–Ti, Cu–Mn–Al and Ni–Al base alloys. The details of those will be reported before long.

Some of the most fascinating points regarding application of this LTE material to the field of electronics can be described as follows: (1) the CTE is changeable in the range from about 0 to $15\times10^{-6}\ K^{-1}$ with the reduction rate of the cold rolling and (2) this Cu–Zn–Al specimen after cold rolling has a relatively high electric conductivity of about 20% IACS. According to the cyclic tests over 500 cycles between -196 and 90 °C for the specimen of 9% cold-rolled reduction, almost the same dilatation curves of Fig. 1 were obtained, which means that the LTE characteristics caused by SI TM can be well reproduced. It has also been confirmed that two-dimensional LTE with LTE$\approx$0 in every direction of the sheet plane can be also obtained by alternately cross rolling as shown in Fig. 3(b). Furthermore, it should be noted

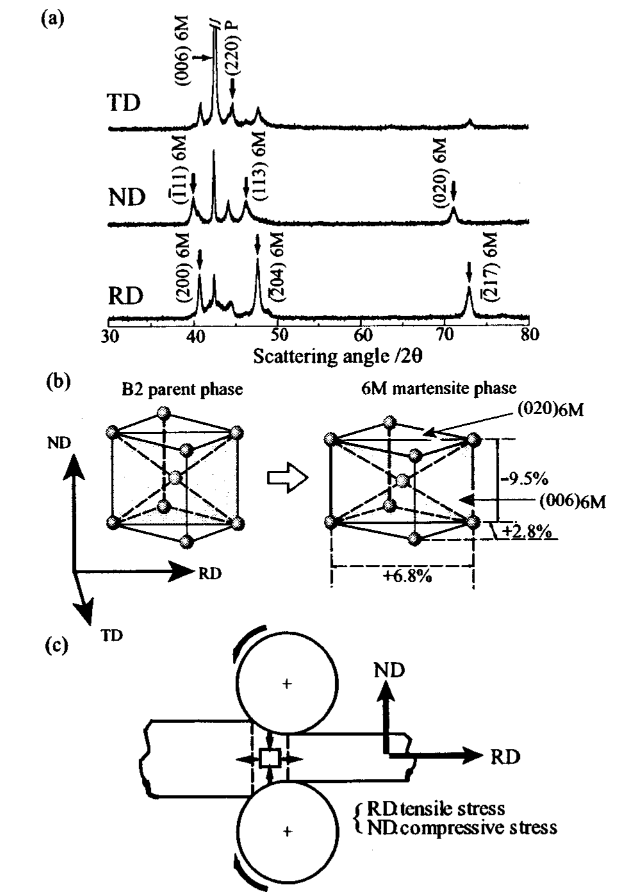

FIG. 4. Martensite texture induced by cold rolling, where (a) XRD patterns were obtained from the TD, ND and RD sections of the 6% cold-rolled specimen. (b) Lattice correspondence between parent martensite phases estimated from the XRD patterns and (c) stress distribution in the cold-rolling area.

that this technique is applicable to obtain materials with extremely high CTE over $30\times10^{-6}\ K^{-1}$ as demonstrated in ND curves of Figs. 3(a) and 3(b). This type of LTE material has high potential for practical applications in such things as electrical parts, micromachines, energy technology, etc.

This work was supported by a Grant-in-Aid for Scientific Research and Development from the Ministry of Education, Science, Sports and Culture of Japan.

[1] Ch. Éd. Guillaume, Proc. Phys. Soc. **32**, 374 (1920).
[2] E. F. Wasserman, in *Ferromagnetic Materials*, edited by K. H. J. Buschow and E. P. Wohlfarth (North-Holland, Amsterdam, 1990), pp. 237–322.
[3] Y. Nakamura, in *Physics and Engineering Applications of Magnetism*, edited by Y. Ishikawa and N. Miura (Springer, Berlin, 1991), pp. 111–132.
[4] H. Saito, in *Physics and Applications of Invar Alloys*, edited by H. Saito *et al.* (Maruzen, Tokyo, 1978), pp. 513–549.
[5] K. Fukamichi and H. Saito, Phys. Status Solidi A **10**, K129 (1972).
[6] M. Mali, Proc. IEEE **73**, 1396 (1985).
[7] J. V. Humbeeck and R. Stalmans, in *Shape Memory Materials*, edited by K. Otsuka and C. M. Wayman (Cambridge University Press, Cambridge, 1998), pp. 149–183.
[8] *Metals Handbook*, 9th ed., edited by D. Wenschhof (American Society for Metals, Metals Park, OH, 1980), Vol. 3, pp. 792–798.
[9] V. I. Zel'dovich, G. A. Sobyanina, and O. S. Rinkevich, Fiz. Met. Metalloved. **81**, 107 (1996); **81**, 305 (1996).
[10] Y. N. Liu and G. S. Tan, Intermetallics **8**, 67 (2000).
[11] Z. K. Lu and G. J. Weng, Smart Mater. Struct. **9**, 582 (2000).
[12] K. Otsuka, T. Ohba, M. Tokonami, and C. M. Wayman, Scr. Metall. Mater. **29**, 1359 (1993).