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Dilatometric behavior of martensitic transformation of $NdNbO_4$ polycrystals

M. OMORI, Y. KOBAYASHI, T. HIRAI
Institute for Materials Research, Tohoku University, 2-1-1 Katahira Aoba-ku, Sendai 980-8577, Japan
E-mail: mamori@imr.tohoku.ac.jp

$NdNbO_4$ is a thermoelastic martensite compound. Dilatation of $NdNbO_4$ polycrystals has not been achieved. Thermal expansion of the $NdNbO_4$ polycrystal was measured with a differential dilatometer at various heating rates and applied loads. Transformation temperatures changed at 10 and 20°C/min according to the uniaxial compression. This change is characteristic of thermoelastic martensitic transformation. The transformation was not altered at 5°C/min. The polycrystal was deformed elastically and broken by the uniaxial compression. © *2000 Kluwer Academic Publishers*

1. Introduction

Martensitic transformation is divided into two types, thermoelastic martensitic transformation and nonthermoelastic transformation, shape memory alloys belonging to the former. Both types of martensitic transformation are induced by stress. The thermoelastic transformation induced by stress is reversible, and the nonthermoelastic is irreversible. Pseudoelasticity is an attribute of thermoelasticity which consists of superelasticity and rubber-like behavior of twin boundary motion. Superelasticity is reversible stress-induced martensitic transformation. The twin boundary motion is reversible non-elastic deformation [1–3].

Toughening of zirconia is achieved by the stress-induced martensitic transformation which is nonthermoelastic. However, tetragonal zirconia polycrystals stabilized by ceria show a stress-strain curve due to pseudoelasticity [4]. It is not clear whether the high toughness of the ceria-doped zirconia depends on thermoelasticity or nonthermoelasticity. Furthermore, it is unknown what the stress-strain curve is based on, superelasticity or rubber-like behavior.

$LnNbO_4$ compounds transform from monoclinic to tetragonal structures [5, 6]. This transformation is martensitic and thermoelastic [7–10]. The $LnNbO_4$ single crystal which contains transformation twins is not deformed elastically. The deformation is similar to what shape memory alloys do [7, 8]. This phenomenon is called rubber-like behavior. The thermal expansion of single crystals of $LaNbO_4$ and $NdNbO_4$ has been conducted at over 800°C by dilatometry [8]. Transformation temperatures of $LnNbO_4$ polycrystals have been measured by X-ray diffraction techniques [7]. It is not easy to grow a single crystal and take a X-ray diffraction pattern at high temperatures. In this paper, the martensitic transformation behavior of $NdNbO_4$ polycrystals is determined by dilatometry and discussed.

2. Experimental

Starting materials were Nd_2O_3 (Santoku Kinzoku Co. Ltd, 99.99%) and Nb_2O_5 (Wako Pure Chemical Ind. Ltd, 99.9%). These powders were dried at 200°C for 48 h and mixed using an agate mortar and pestle for 20 min. The mixture of Nd_2O_3 and Nb_2O_5 was put in a graphite die (50 mm diameter), set in a spark plasma system (Sumitomo Coal Mining, Co. Ltd, SPS 1050), and then sintered at 20 MPa in a vacuum. The sintering temperature and time were determined as follows: 20–1150°C for 15 min and 1150°C for 3 min.

The sintered sample was polished and cut for measurements. The thermal expansion of prismatic specimens ($3 \times 4 \times 20$ mm^3) was determined by a differential dilatometer (Mac-Science, TD5200) using an alumina bar as a standard from 20 to 1000°C at various heating and cooling rates of 5, 10, and 20°C/min at applied compressions in air. The load applied to specimens was from 1×10^3 Pa to 1×10^5 Pa. A uniaxial compression test was done using a universal testing machine (Instron, TT-CM-L) to take a stress-strain loop. Dimensions of the specimen were 2.81×5.38 mm^2 and the strain rate was 0.005 mm/min.

3. Results

Dilatation of $NdNbO_4$ polycrystals was determined at various heating rates and applied compressions. Fig. 1 shows one of the thermal expansion curves of the sintered $NdNbO_4$ polycrystal taken at a load of 1×10^3 Pa and a heating rate of 20°C/min. All other curves were similar to it. There was no clear volume change due to the transformation from monoclinic to tetragonal structures. The thermal expansion changed at temperatures of A (reverse transformation) and M (martensitic transformation) on heating and cooling. Transformation temperatures are summarized in Tables I–III. After

TABLE I Transformation temperatures at 20°C/min

Load (Pa)	A_1^a (°C)	M_1^b (°C)	A_2^c (°C)	M_2^d (°C)
1.04×10^3	760	726	761	726
5.44×10^4	746	724	743	722
1.05×10^5	736	723	732	723

[a] Reverse transformation temperature on first measurement.
[b] Martensitic transformation temperature on first measurement.
[c] Reverse transformation temperature on second measurement.
[d] Martensitic transformation temperature on second measurement.

TABLE II Transformation temperatures at 10°C/min

Load (Pa)	A_1 (°C)	M_1 (°C)	A_2 (°C)	M_2 (°C)	A_3 (°C)	M_3 (°C)
1.03×10^3	733	729	736	727	736	727
1.05×10^5	731	722	731	720	—	—

TABLE III Transformation temperatures at 5°C/min

Load (Pa)	A_1 (°C)	M_1 (°C)	A_2 (°C)	M_2 (°C)
1.05×10^3	732	724	731	724
1.07×10^5	730	725	728	725

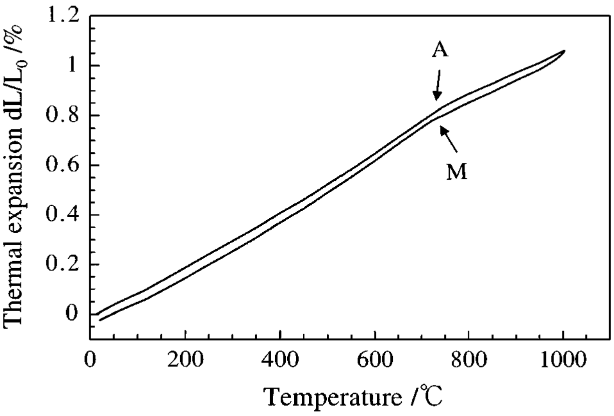

Figure 1 Thermal expansion of $NdNbO_4$ polycrystal.

the first measurement was done using a sample which was sintered and not annealed, the second and third ones were carried out continuously. The transformation temperature did not differ for the second and the third, as shown in Table II. When the heating rate was faster than 10°C/min, the transformation was altered by the uniaxial compression. The polycrystals were transformed in a small temperature range at 5°C/min. The experimental error of the transformation temperature was about ±0.5°C. The pressure effect on M was different between the fast heating rate (10 and 20°C/min) and the slow (5°C/min).

The stress-strain loop of compression is shown in Fig. 2. The polycrystal of $NdNbO_4$ was deformed elastically and fractured. Pseudoelasticity was not observed for the polycrystal.

4. Discussion

Transformation temperatures of zirconia are described as Ms (martensite-start temperature on cooling), Mf (martensite-finish temperature), As (reverse transformation-start temperature on heating) and Af (reverse transformation-finish temperature) [11]. $Y_4Al_2O_9$ has the same transformation behavior [12]. Fig. 1 shows that the transformation is not divided into start and finish temperatures. The thermal expansion change of a single crystal is gradual and continuous in the absence of steep volume change, and indicates that the phase transformation is second order [8]. This continuous change is attributed to thermoelasticity. There are a lot of twins in the monoclinic phase of zirconia. However, the twins do not result in high toughness of monoclinic zirconia. The twin of $Y_4Al_2O_9$, which is a martensite compound, acts as a defect and rather decreases the strength and toughness of SiC-$Y_4Al_2O_9$ composites [13]. The volume change of zirconia and $Y_4Al_2O_9$ is steep and discontinuous, perhaps indicating nonthermoelasticity.

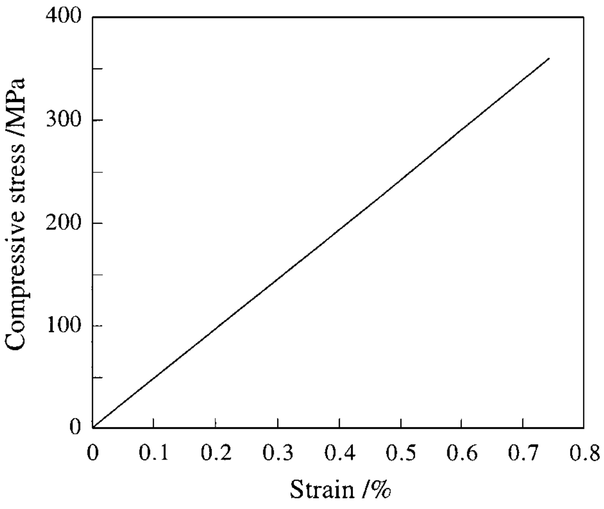

Figure 2 Stress-strain curve of $NdNbO_4$ polycrystal.

The sintered sample was annealed by the first measurement of the thermal expansion, because the second did not result in the same temperature. The temperature in the third round was same as in the second, as shown in Table II. Annealing is necessary to relax the stress accumulated in a sintering process.

The thermoelastic martensitic transformation is regulated by temperatures and stress. Ms is raised, but Mf are lowered by uniaxial compression. In this case, the stress and pressure are imposed at various temperature levels, maintained at ±0.5°C [14]. The thermoelastic transformation is gradual, and the transformation process can be observed [7]. The slow transformation is perhaps influenced by the heating rate. M is considered to consist of Ms and Mf. At fast heating of Table I, M is lowered by the uniaxial pressure such as Mf, and may be mainly influenced by the Mf component. M seems to be raised at 5°C/min. However, the temperature difference is near the limits of experimental error. The Ms component increases in M at slow heating. Raising Ms may compensate for lowering of Mf, and the fluctuation of transformation temperatures becomes small. The M temperature of a single crystal is 725°C which is the same as that at 5°C/min [8].

The twin boundary of the $NbNdO_4$ single crystal is deformed reversibly by uniaxial stress [9]. In a polycrystal, directions of the twin boundary are not aligned and there are not spaces where the twin boundary can move. Fig. 2 shows that there is no indication that the twin is mobile at the boundary. The boundary should be allowed to be deformed in the ceramic matrix, the thermal expansion coefficients of which are less than that of $NbNdO_4$; the rubber-like behavior may be able to afford the ceramic composites with high toughness.

5. Conclusion

The thermal expansion behavior of thermoelastic $NdNbO_4$ polycrystals was examined using a differential dilatometer. The applied load was varied from 10^{-3} to 10^{-5} Pa. The heating rate was from 5 to 20°C/min. The transformation temperature (M) was lowered at 10 and 20°C/min by the uniaxial compression, but did not change at 5°C/min. The measurement of the dilatation at the slow heating rate such as 5°C/min is recommended to permit comparison of transformation temperatures.

The twin boundary is hardly moved in polycrystals by stress. Composites should be formed from the matrix with less thermal expansion coefficients in order to utilize rubber-like behavior.

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