JOURNAL OF MATERIALS SCIENCE **38** (2003) 869–876

Effects of microstructure and environment on room-temperature tensile properties of B2-type polycrystalline CoTi intermetallic compound

YASUYUKI KANENO*, TAKAYUKI TAKASUGI
Department of Metallurgy and Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan
E-mail: kaneno@mtl.osakafu-u.ac.jp

Room-temperature tensile property and fracture mode of B2-type polycrystalline CoTi intermetallic compound was studied as functions of microstructure and environment. Using a hot-rolled CoTi sheet, various microstructures were prepared by different heat treatments and pre-straining. Tensile elongation as well as ultimate tensile strength (UTS) of specimens deformed in vacuum (i.e. intrinsic tensile elongation and strength) depended on microstructure. The hot-rolled and recovered specimens showed higher elongation and tensile strength than the fully-annealed and aged specimens. Also, the pre-strained specimen showed the improved elongation and UTS in comparison with the fully-annealed specimen. On the other hand, tensile elongation and UTS of the specimens deformed in air were lower than those of the specimens deformed in vacuum, irrespective of microstructure. The extent of embrittlement was lower in the hot-rolled, recovered and pre-strained specimens than in the fully-annealed and aged specimens. SEM observation for the hot-rolled and recovered specimens showed that the quasi-cleavage fracture mode was dominant irrespective of testing environment. However, the fully-annealed, aged and pre-strained specimens consisting of recrystallized grains exhibited quasi-cleavage fracture mode mixed with intergranular fracture mode. The results showed that not only the intrinsic room-temperature tensile properties but also the environmental embrittlement of CoTi intermetallic compound depended upon lattice defects (such as dislocations and vacancies) in addition to grain size and morphology.

1. Introduction

B2-type ordered intermetallic compounds have generally high melting point and high ordering energy, and show high strength, good corrosion resistance and high phase stability. Among many B2-type ordered intermetallic compounds, CoTi is stable up to melting point [1], and also shows a positive temperature dependence of yield strength [2]. Recently, the temperature dependence of tensile property and fracture mode for the hot-rolled and recrystallized CoTi was investigated by the present authors [3]. Consequently, polycrystalline CoTi was found to show fair deformability at elevated temperatures.

The room-temperature ductility of the B2-type strongly-ordered intermetallic compounds is generally low. The poor ductility is considered to come from the intrinsic brittleness due to the difficulty of slip deformation in the B2 ordered structure. The intrinsic brittleness of ordered intermetallic compounds as well as metallic materials may be improved by microstructure control. To prepare the desired microstructures, recent studies for B2-type FeAl-based ordered alloys have been focusing on the alloying [4] and processing [5, 6]. Also, it has been reported that grain refinement by mechanical alloying is useful to improve room-temperature ductility of NiAl [7]. On the other hand, many ordered intermetallic compounds have been suffering from the moisture-induced embrittlement in air at ambient temperature. For example, $L1_2$-type ordered alloys such as Co_3Ti [8], $Ni_3(Si,Ti)$ [9, 10] and Ni_3Al [11] are embrittled in air, resulting in reduction of tensile elongation and fracture strength. Also, recent studies have shown that the moisture-induced embrittlement in Co_3Ti and $Ni_3(Si,Ti)$ alloys is greatly influenced by microstructure, such as grain size [12, 13] and the existence of second phase [14]. For B2-type ordered intermetallic compounds, it has been known that FeAl-based alloys show the moisture-induced embrittlement at ambient temperature [15–19]. However, the room-temperature mechanical properties including the moisture-induced embrittlement for B2-type CoTi intermetallic compound have not been studied so far. The improvement of room-temperature mechanical properties of CoTi intermetallic compound is expected by microstructure control.

---

[*] Author to whom all correspondence should be addressed.

To obtain different kind of microstructures which have various grain sizes and morphology, and also contain various contents of lattice defects (such as dislocations and vacancies), B2-type polycrystalline CoTi intermetallic compound with a stoichiometric composition was hot-rolled, and subsequently annealed and redeformed. Tensile tests were conducted at room temperature in vacuum and air. Fracture behavior was observed using scanning electron microscope (SEM). Based on these results, the effects of microstructure and environment on room-temperature tensile properties of CoTi ordered intermetallic compound was discussed.

2. Experimental procedures

Raw materials used in this study were 99.9wt% cobalt and 99.9wt% titanium. A stoichiometric Co-50at.%Ti alloy was prepared by arc melting in an argon gas atmosphere on a copper hearth using a non-consumable tungsten electrode. Homogenization heat treatment was conducted in vacuum at 1473 K for 48 h, followed by furnace cooling. A homogenized ingot was sheathed with stainless steel, and then hot-rolled at 1273 K in air to approx. 80% reduction in thickness. Final thickness of the sheet was approximately 2 mm. Test pieces for tensile tests were cut from the hot-rolled sheet by an electro-discharge machine (EDM). The surfaces of tensile test pieces were mechanically ground and finally buffed to 1 mm thickness to eliminate damaged surface layers. Annealing was conducted at 873 K and 1323 K for 10 h, followed by furnace cooling at a cooling rate of ∼300 K/h. The annealing treatments at 873 K and at 1323 K were intended to obtain recovered and fully-recrystallized microstructures, respectively. To investigate the effect of the elimination of thermal vacancy on tensile properties, a heat treatment at 673 K for 96 h was conducted, using the specimen preceded by an annealing at 1323 K for 10 h. This low-temperature and long-term annealing is, for convenience, named *aging* in the followings. The previous study reported that the fully-recrystallized CoTi intermetallic compound shows tensile elongation more than 20% at temperatures beyond 873 K [3]. Therefore, the fully-annealed (recrystallized) specimen that was tensile deformed at 873 K to ∼5% strain was prepared as a pre-strained specimen. The thermomechanical treatment used to prepare various microstructures is schematically illustrated in Fig. 1. The grain structures were observed by an optical microscope after etching in a solution of 2.5% HF, 2.5% HNO_3 and 95% H_2O. Tensile tests were conducted in either vacuum (6.7×10^{-4}–9.3×10^{-3} Pa) or air at room temperature (∼300 K) at an initial strain rate of $1.6 \times 10^{-3}\ s^{-1}$. Fracture surfaces of tensile deformed specimens were examined by a scanning electron microscope (SEM). Also, the deformation marking was observed on the surface of the tensile-deformed specimen by optical microscopy.

3. Results and discussions

3.1. Microstructure and hardness

Fig. 2 shows optical micrographs of hot-rolled and annealed specimens. The *hot-rolled* specimen appears to retain the deformed microstructure in spite of the high-temperature (1273 K) rolling (Fig. 2a). For the *recovered* specimen annealed at 873 K for 10 h, an unrecrystallized microstructure can be recognized (Fig. 2b). The

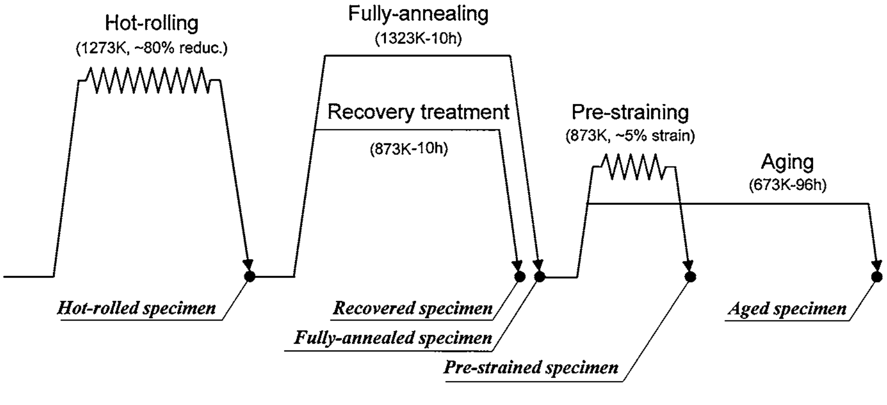

Figure 1 Schematic illustration of thermomechanical treatment by which the samples were prepared in this study.

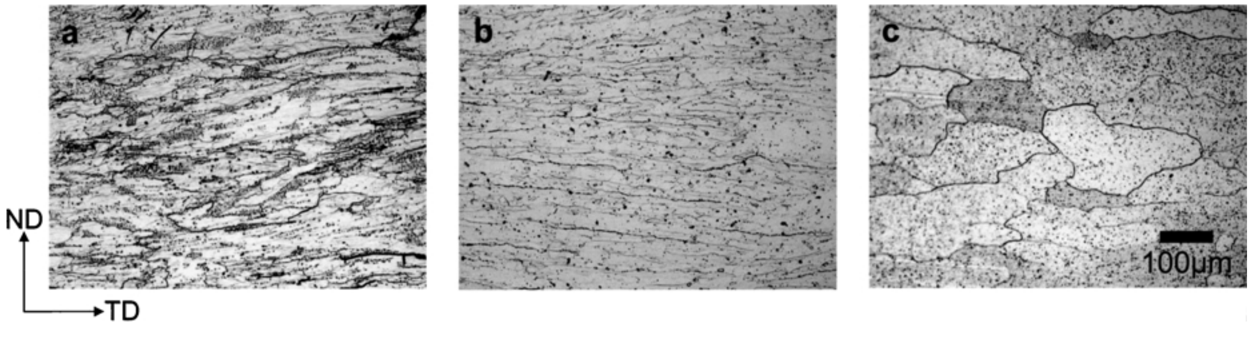

Figure 2 Optical micrographs of (a) hot-rolled, (b) recovered, and (c) fully-annealed specimens (ND: normal direction, TD: transverse direction).

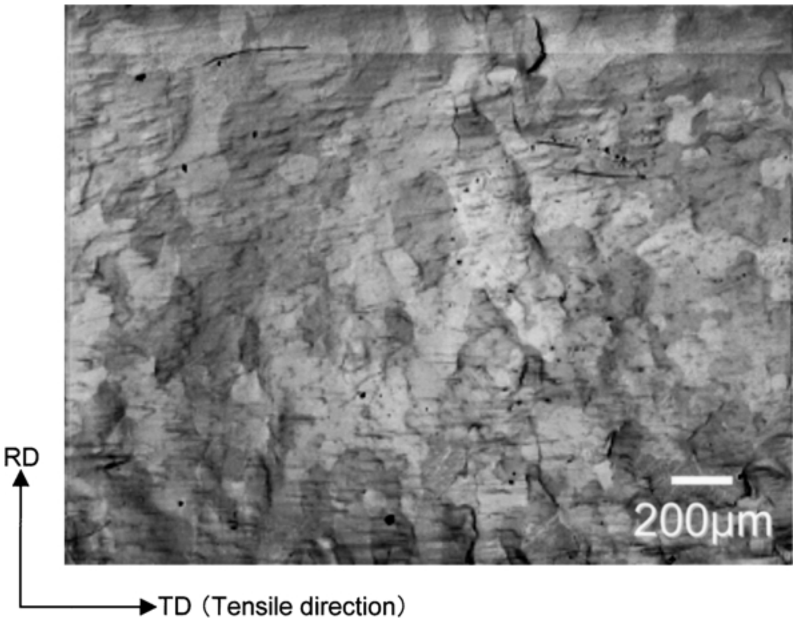

Figure 3 Optical micrograph of the pre-strained specimen (RD: rolling direction, TD: transverse direction). Pre-straining was conducted at 873 K to ∼5% strain using the fully-annealed specimen. Note that the observed plane in this figure is different from that in Fig. 1.

fully-annealed specimen (annealed at 1323 K for 10 h) shows a fully-recrystallized microstructure (Fig. 2c). Also, the *aged* specimen showed similar microstructure to the fully-annealed specimen. Fig. 3 shows an optical micrograph of the pre-strained specimen that was thermally etched by tensile deformation at 873 K in vacuum. It is evident that grain size and morphology in the pre-strained specimen are primarily similar to those in the fully-annealed specimen. Corresponding to these microstructures, the microhardness of the hot-rolled and recovered specimens is higher than that of the fully-annealed specimen, as shown in Fig. 4. For the recovered specimen, the hardness is slightly lower than that of the hot-rolled specimen, indicating that recovery takes place at 873 K. In Fig. 4, the hardness of the aged specimen is also included. It is found that the low-temperature and long-term annealing, which is aimed to eliminate thermal vacancies generated at a high temperature and/or retained during furnace cooling, causes no change in hardness in comparison with the fully-annealed specimen. This indicates that the thermal vacancies in CoTi are little introduced by the high temperature annealing, or they hardly affect the hardness.

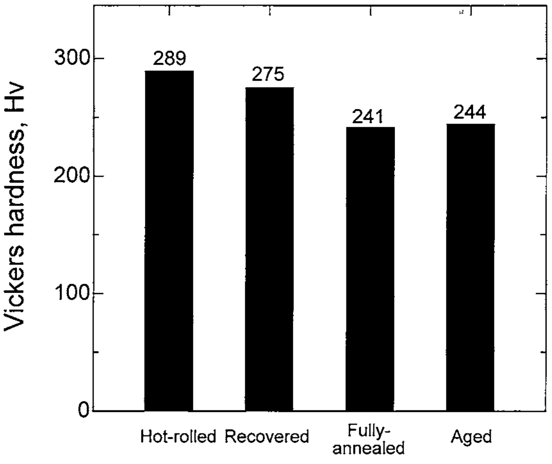

Figure 4 Vickers hardness of specimens with various kinds of microstructures.

3.2. Tensile property in vacuum

Fig. 5 represents typical nominal stress versus nominal strain curves for the hot-rolled and fully-annealed specimens, which were tensile deformed in vacuum and air, respectively. Irrespective of testing environment, the tensile strength of the hot-rolled specimen is higher than that of the fully-annealed specimen. These figures also indicate that the reproducibility of the stress-strain curves in each microstructure and environment is appreciably good.

Tensile elongation, ultimate tensile strength (UTS) and yield strength (0.2% proof strength) of specimens deformed in vacuum as well as in air are plotted in Fig. 6. Elongation in this figure corresponds to plastic strain to fracture. Also, the elongation of ∼5% given by the pre-straining at 873 K is not added to the elongation value measured in the pre-strained specimen shown in Fig. 6. The data shown in each specimen condition are the average of at lease twice of tensile tests. The aged specimen tensile deformed in air fractured before yielding. CoTi intermetallic compound showed low but certain levels of tensile ductility at room temperature, though most B2-type ordered intermetallic compounds generally show a very limited ductility at room temperature.

Describing the results (i.e. intrinsic properties) of the specimens deformed in vacuum, tensile elongation apparently depends on microstructure. The specimens with unrecrystallized microstructure (i.e. the hot-rolled and recovered specimens) show higher elongation than the specimens with microstructure consisting of recrystallized grains (i.e. the fully-annealed and aged specimens). On the other hand, the pre-strained specimen

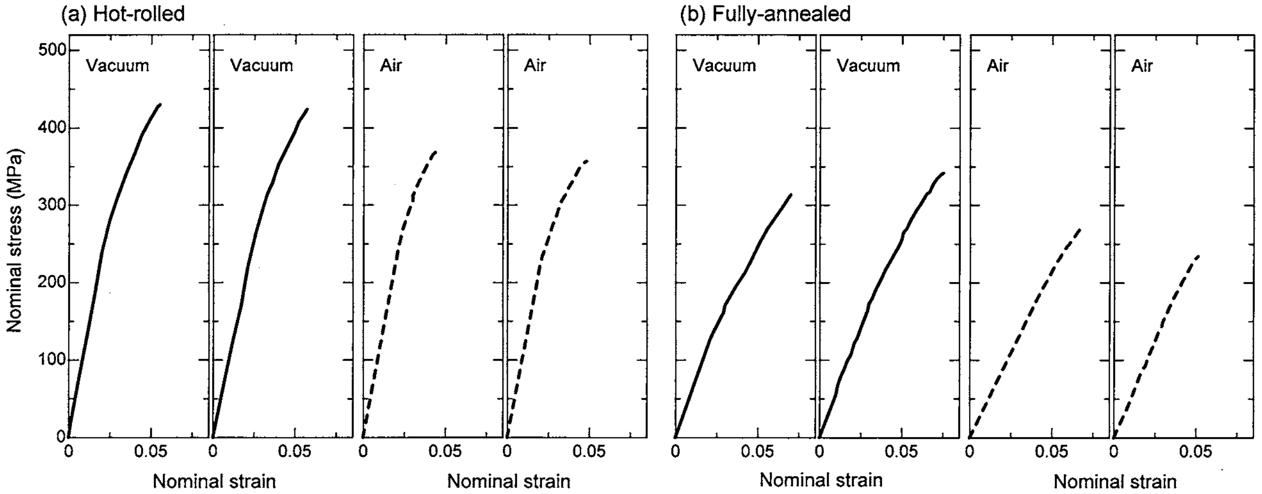

Figure 5 Nominal stress-strain curve of (a) hot-rolled and (b) fully-annealed specimens. Tensile tests were conducted in air and vacuum, respectively.

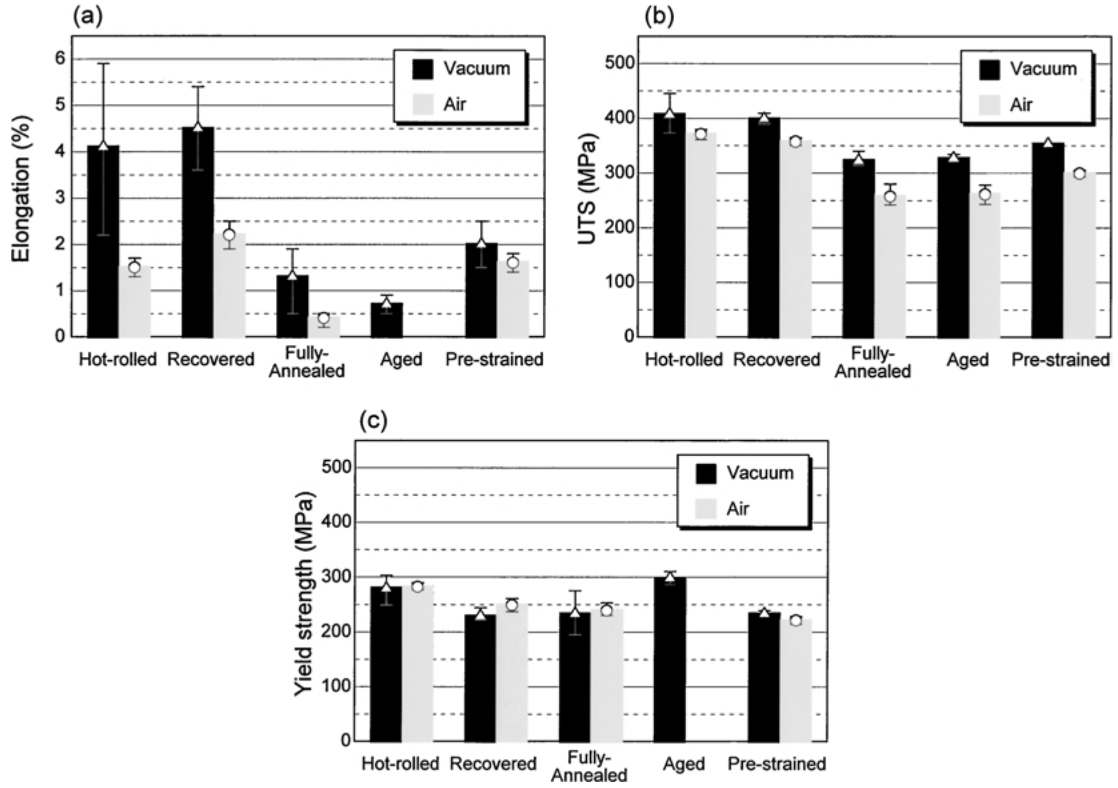

Figure 6 Room-temperature tensile properties of specimens with various microstructures; (a) elongation, (b) ultimate tensile strength and (c) yield stress.

shows higher elongation than the fully-annealed and aged specimens. It is also apparent that UTS depends on the microstructure in the same way that the tensile elongation behaves. However, yield strength seems to be primarily insensitive to the microstructure.

For CoTi intermetallic compound, the poor ductility at room temperature is possibly due to the facts that the active slip system at low temperatures is {110}⟨001⟩ [20, 21] and therefore the number of slip systems guaranteeing the von Mises' criterion is not satisfied. In addition, the stress driving dislocations is very high and the multiplication of ⟨001⟩ dislocations may be difficult. However, if introducing mobile dislocations into the material, there is a possibility that ductility at low temperatures can be improved [22, 23]. In the present study, deformed microstructure was retained in the hot-rolled specimen (Fig. 1), and showed higher hardness than fully-recrystallized microstructure. Therefore, the dislocation density is assumed to be higher in the hot-rolled specimen than in the fully-annealed specimen. Consequently, the hot-rolled specimen showed higher elongation (and UTS) than the fully-annealed specimen. Also, it is suggested that pre-straining introduces the mobile dislocations into the specimen and can increase elongation of the fully-annealed specimen, as shown in Fig. 6. Concerning the recovered specimen, it is suggested that dislocations still remain and their distribution might be rearranged by polygonization. Namely, dislocations in the recovered specimen are expected to be more mobile than those in the hot-rolled specimen. Dislocations as well as vacancies might further decrease in the aged specimen, and thereby the aged specimen might show the lowest elongation among the prepared specimens (microstructures). Grain size might also affect the ductility of CoTi. The deformation of the fully-annealed specimen with quite larger grain size than those of the hot-rolled and recovered specimens proceeded inhomogeneously, resulting in a low level of elongation. Also, stepped (ledged) grain boundaries observed in the hot-rolled and recovered specimens may be effective to suppress intergranular fracture. Moreover, there is a possibility that the crystallographic texture affects the ductility. To furthermore clarify the effect of microstructure on room-temperature mechanical property of CoTi intermetallic compound, more experiments including TEM observation and texture measurement are required.

3.3. Environmental effect on tensile property

Fig. 6 clearly shows that yield strength is insensitive to the testing environment as well as microstructure. However, the tensile elongation and the ultimate tensile strength (UTS) are apparently dependent on the environment (Figs 5 and 6). For the hot-rolled specimen, the elongation of the specimen tested in air is lower than that of the specimen tested in vacuum, as shown in Fig. 6. As well as the elongation, UTS is lower in the specimens tested in air than the specimens tested in vacuum. The same environmental dependence of tensile properties can be recognized in other microstructures. These results clearly indicate that moisture-induced embrittlement takes place in CoTi intermetallic compound, as have been observed in many ordered intermetallic compounds.

It has been suggested that the environmental embrittlement of ordered intermetallics is induced by decomposition of moisture in air on alloy surface, resulting in generation of atomic hydrogen. Since CoTi contains titanium as a reactive element, moisture in air can be decomposed into atomic hydrogen according to a reaction $Ti + 2H_2O \rightarrow TiO_2 + 4H$. By the subsequent absorption and migration of atomic hydrogen at a propagating crack tip in lattice or grain boundary, moisture-induced embrittlement in CoTi is caused as well as in other intermetallic compounds.

3.4. Microstructural effect on moisture-induced embrittlement

The moisture-induced embrittlement occurs irrespective of the microstructure, but the ratios of the elongation and UTS in air to those in vacuum (namely, the extent of embrittlement) appear to be dependent on microstructure. Fig. 7 shows the reduction of the elongation and UTS for the specimens with various kinds of microstructures. In this figure, the reduction of the elongation (and UTS) was defined as $R(\%) = (\varepsilon_{\mathrm{Vacuum}} - \varepsilon_{\mathrm{Air}}) \cdot 100/\varepsilon_{\mathrm{Vacuum}}$. Here, $\varepsilon_{\mathrm{Vacuum}}$ and $\varepsilon_{\mathrm{Air}}$ represent the elongation values in vacuum and air, respectively. For both the elongation and UTS, the large reduction is found in the fully-annealed and aged specimens among the prepared microstructures. This implies that the fully-recrystallized microstructure most seriously suffers from moisture-induced embrittlement. Here, it is noted that the pre-straining is effective in suppressing the moisture-induced embrittlement. On the other hand, the hot-rolled and recovered specimens exhibit intermediate values of the reduction of the elongation (and UTS) among the prepared microstructures.

Previous studies for the $L1_2$-type $Ni_3(Si,Ti)$ alloy showed that the embrittlement was reduced by the pre-straining [24] or shot-peening [25]. These results indicate that dislocations (or vacancies) introduced by the pre-straining or shot-peening interact with atomic hydrogen, resulting in the beneficial effect of reducing the embrittlement. In the present study, the dislocation density in the hot-rolled and pre-strained specimens (probably, even in the recovered specimen) is considered to be higher than that in the fully-annealed specimen, as described in the previous section. Therefore, it is suggested that the retained or introduced dislocations (or vacancies) act as a trap site of hydrogen and reduce the hydrogen content arriving at grain boundaries or in lattice defects in front of a propagating micro cracks, resulting in reducing the extent of the embrittlement.

Recently, it has been found that the environmental embrittlement of the recrystallized $L1_2$-type Co_3Ti [12] and $Ni_3(Si,Ti)$ [13] ordered alloys depends on grain size. It was reported that ductile-brittle transition (DBT) occurs at lower strain rate as the grain size decreases. Namely, grain refinement was shown to be a useful method by which the moisture-induced embrittlement can be reduced [12, 13]. The proposed mechanism responsible for the grain size effect on the DBT for

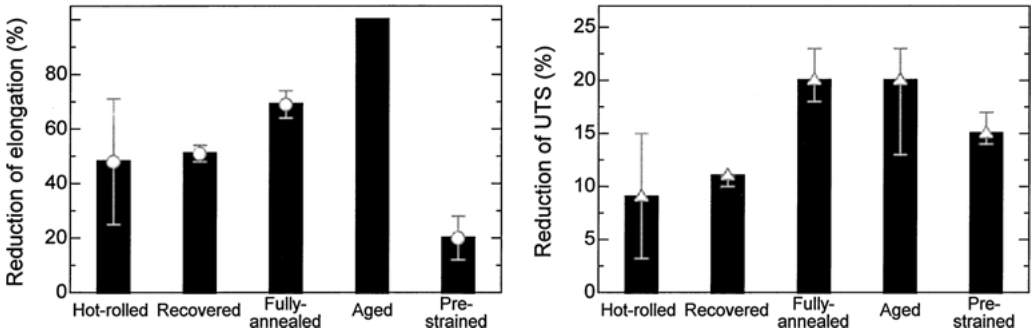

Figure 7 The reduction of (a) the elongation and (b) UTS for specimens with various kinds of microstructures, showing the extent of the embrittlement.

$L1_2$-type ordered alloy is as follows [12]. A fine grained microstructure with a large area of grain boundary reduces the concentration of atomic hydrogen residing in grain boundaries. As a result, atomic hydrogen residing in grain boundaries of the materials consisting of fine grain microstructure can not exceed its critical hydrogen concentration above which grain boundary fracture occurs. Assuming that grain boundaries similarly act as trap sites of hydrogen in B2-type CoTi intermetallic compound, deformed and recovered microstructures are expected to be more effective in suppressing of the moisture-induced embrittlement because they are composed of fine, elongated and stepped (ledged) grains. Stepped (ledged) grain boundaries are expected to provide more trap sites of hydrogen than flat (smoothed) grain boundaries.

It is assumed that CoTi intermetallic compound as well as FeAl and NiAl intermetallic compounds [26–28] contains high concentration of vacancies at elevated temperature and are retained at low temperature, although the measured hardness was not so much affected by retained thermal vacancies. Assuming that retained thermal vacancy has the effect of trapping and scavenging the absorbed hydrogen, the reduced moisture-induced embrittlement is not expected in the aged microstructure but expected in other microstructures that were not vacancy-eliminated. Actually, it has been shown that the worst moisture-induced embrittlement took place in the aged specimen.

3.5. Fractography

Fig. 8 shows SEM fractographies for the tensile-deformed specimens. All the specimens exhibit brittle fracture modes, corresponding to low ductility at room temperature. Quasi-cleavage fracture is primarily dominant, irrespective of testing microstructure and environment. In the case of $L1_2$-type ordered intermetallic alloys such as Co_3Ti and $Ni_3(Si,Ti)$ which have somewhat ductility at room temperature, when environmentally embrittled, fracture mode changes from ductile transgranular fracture to brittle intergranular fracture [8, 29]. Atomic hydrogen in these cases has been suggested to affect grain boundaries, resulting in decrease in grain boundary cohesion. In the case of B2-type intermetallic compounds which are intrinsically brittle at room temperature because of their lower cleavage strength than grain boundary strength, it is suggested that atomic hydrogen causes further reduction of lattice strength, resulting in the cleavage fracture.

The specimens consisting of recrystallized grains, i.e. the fully-annealed, aged and pre-strained specimens showed intergranular fracture mode in addition to quasi-cleavage fracture mode in both air and vacuum, indicating that fracture behavior is influenced by microstructure, but basically not by environment.

The optical microscopy on the surfaces of the hot-rolled and fully-annealed specimens after tensile deformation is shown in Fig. 9. Fine slip lines are observed for the hot-rolled specimen, while only limited coarse slip lines are observed for the fully-annealed specimen, irrespective of testing environment. For the fully-annealed specimen, it appears that intergranular fracture is introduced when slip deformation is not so efficiently activated in the neighboring grains (Fig. 9d). This result suggests that stress is concentrated at grain boundaries consisting of recrystallized coarse grains, resulting in intergranular fracture.

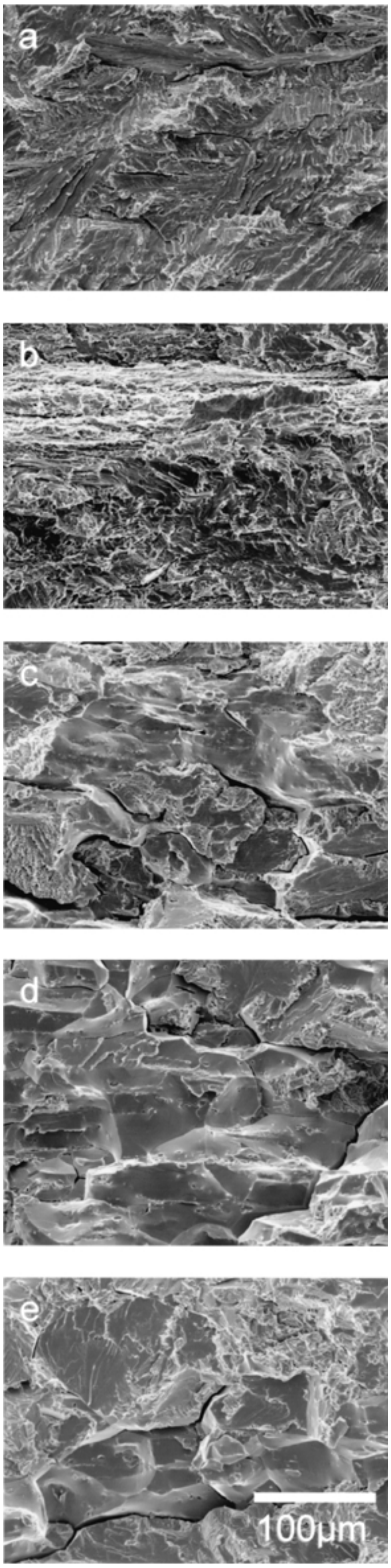

Figure 8 SEM fractographies of (a) hot-rolled, (b) recovered, (c) fully-annealed, (d) aged and (e) pre-strained specimens. Observations were conducted on the specimens tensile deformed in vacuum.

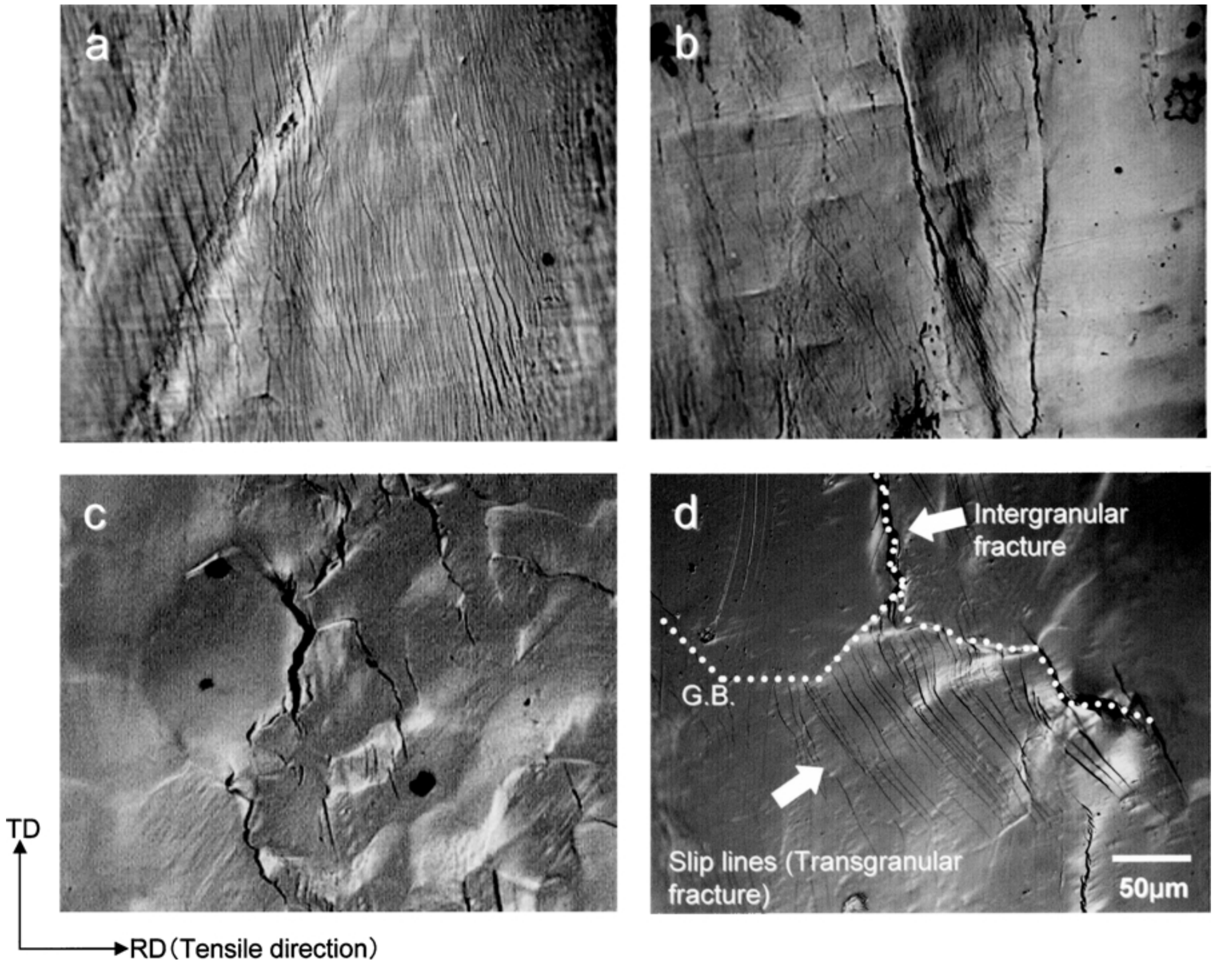

Figure 9 Optical micrographs of (a, b) hot-rolled and (c, d) fully-annealed specimens, respectively (RD: rolling direction, TD: transverse direction). Observations were conducted on the specimens tensile deformed in (a, c) vacuum and (b, d) air, respectively.

4. Conclusion

B2-type polycrystalline CoTi intermetallic compound with various microstructures was tensile tested at room temperature in vacuum and air. The following results were obtained from the present study.

(1) For the room-temperature tensile properties in vacuum, the hot-rolled and recovered specimens (i.e. unrecrystallized microstructure) showed higher elongation and UTS than the fully-annealed and age specimens (i.e. fully-recrystallized microstructure). Also, pre-straining improved the elongation and UTS in comparison with the fully-annealed specimen.

(2) Irrespective of microstructure, the tensile elongation and UTS in air were lower than those in vacuum, indicating that the moisture-induced embrittlement occurred in CoTi intermetallic compound.

(3) The extent of embrittlement was lower in the hot-rolled, recovered and pre-strained specimens than in the fully-annealed and aged specimens, suggesting that the moisture-induced embrittlement in CoTi intermetallic compound is greatly affected by retained deformed microstructure.

(4) All the specimens showed that quasi-cleavage fracture mode was primarily dominant irrespective of testing microstructure and environment. However, the fully-annealed, aged and pre-strained specimens consisting of recrystallized grains exhibited intergranular fracture mode in addition to quasi-cleavage fracture mode in both vacuum and air.

(5) The results obtained suggest that deformed microstructure, i.e. lattice defects (such as dislocations and vacancies) in addition to grain size and morphology, affects not only intrinsic room-temperature tensile property but also extrinsic one (i.e. moisture-induced embrittlement) of CoTi intermetallic compound.

Acknowledgements

This work was supported in part by the Functions of Hydrogen in Environmental Degradation of Structural Materials from the Special Coordination Funds for Promoting Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology, and by the inter-university cooperative research program of the Institute for Materials Research, Tohoku University.

References

1. T. TAKASUGI and O. IZUMI, *Phys. Stat. Sol.* (a) **102** (1987) 697.
2. *Idem.*, *J. Mater. Sci.* **23** (1988) 1265.
3. Y. KANENO, T. TAKASUGI and S. HANADA, *Mater. Sci. Eng.* **A302** (2001) 215.
4. N. S. STOLOFF and C. T. LIU, *Intermetallics* **2** (1994) 75.
5. M. R. HAJALIGOL, S. C. DEEVI, V. K. SIKKA and C. R. SCOREY, *Mater. Sci. Eng.* **A258** (1998) 249.

6. D. J. ALEXANDER, P. J. MAZIASZ and J. L. WRIGHT, *ibid.* **A258** (1998) 276.
7. A. DOLLAR, S. DYMEK and M. DOLLAR, *Archives of Metall.* **47** (2002) 3.
8. T. TAKASUGI and O. IZUMI, *Acta Metall.* **34** (1986) 607.
9. T. TAKASUGI, H. SUENAGA and O. IZUMI, *J. Mater. Sci.* **26** (1991) 1179.
10. T. TAKASUGI, T. NAKAYAMA and S. HANADA, *Mater. Trans. JIM* **34** (1993) 775.
11. C. T. LIU, *Scripta Metall. Mater.* **27** (1992) 25.
12. T. TAKASUGI and S. HANADA, *Scripta Mater.* **41** (1999) 175.
13. Y. KANENO, M. WADA, H. INOUE and T. TAKASUGI, *Mater. Trans.* **42** (2001) 418.
14. T. TAKASUGI, M. WADA, Y. KANENO and H. INOUE, *Mater. Sci. Eng.* A, **329–331** (2002) 523.
15. C. T. LIU, E. H. LEE and C. G. MCKAMEY, *Scripta Metall.* **23** (1989) 875.
16. R. J. LYNCH, K. A. GEE and L. A. HELDT, *ibid.* **30** (1994) 945.
17. M. V. NATHAL and C. T. LIU, *Intermetallics* **3** (1995) 77.
18. W. C. LUU and J. K. WU, *J. Mater. Sci.* **35** (2000) 4121.
19. D. WU and I. BAKER, *Intermetallics* **9** (2001) 57.
20. T. TAKASUGI, K. TSURISAKI, O. IZUMI and S. ONO, *Philos. Mag. A* **61** (1990) 785.
21. T. TAKASUGI, M. YOSHIDA and T. KAWABATA, *ibid. A* **65** (1992) 29.
22. J. E. HACK, J. M. BRZESKI and R. DAROLIA, *Scripta Mater.* **34** (1996) 1633.
23. J. R. KNIBLOE, R. N. WRIGHT, C. L. TRYBUS and V. K. SIKKA, *J. Mater. Sci.* **28** (1993) 2040.
24. C. L. MA, T. TAKASUGI and S. HANADA, *Scripta Mater.* **34** (1996) 1633.
25. *Idem.*, *ibid.* **34** (1996) 1131.
26. P. NAGPAL and I. BAKER, *Metall. Trans.* **21A** (1990) 2281.
27. M. A. MORRIS, O. GEORGE and D. G. MORRIS, *Mater. Sci. Eng.* **A258** (1998) 99.
28. H. XIAO and I. BAKER, *Acta metal. Mater.* **43** (1995) 391.
29. C. L. MA, T. TAKASUGI and S. HANADA, *Mat. Res Soc. Symp. Proc.* **364** (1995) 1159.

Received 20 June
and accepted 21 November 2002