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LOW-TEMPERATURE AGING AND PHASE STABILITY OF U6Nb

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ABSTRACT

Aging behavior and phase stability of a water-quenched U-6wt%Nb (U-14at%Nb) alloy artificially aged at 200°C and naturally aged at ambient temperature for 15 years have been investigated using Vickers hardness test, X-ray diffraction analysis, and transmission electron microscopy techniques. Age hardening/softening phenomenon is observed from the artificially aged samples according to microhardness measurement. The age hardening can be rationalized by the occurrence of spinodal decomposition, or fine scale of Nb segregation, which results in the formation of a nano-scale modulated structure within the artificially aged samples. Coarsening of the modulated structure after prolonged aging leads to the age softening. The occurrence of chemical ordering (disorder-order transformation) is found in the naturally aged sample based upon the observations of antiphase domain boundaries (APB's) and superlattice diffraction patterns. A possible superlattice structure is accordingly proposed for the chemically ordered phase observed in the naturally aged alloy sample.

INTRODUCTION

It is well known that U-6wt%Nb (U6Nb hereafter) alloy is exploited for a variety of engineering applications with a microstructure containing martensitic phases supersaturated with Nb, which can be obtained by rapid quenching the alloy from γ (bcc)-field solid solution to room temperature [1, 2]. The high cooling rate forces the γ -phase solid solution to transform martensitically to a variant of the low temperature α (orthorhombic) phase in which Nb is retained in supersaturated solid solution. Because the variant phase is supersaturated and its lattice parameters differ from the equilibrium α phase, it has been designated α' martensite. Two additional variant phases, a monoclinic distortion of α' , named α'' martensite or a tetragonal distortion of γ , named γ^o martensite, can also be formed within the as-quenched material. The resulting alloy has improved mechanical properties (ductility and toughness) and excellent corrosion resistance because of the uniform distribution of Nb in solid solution that suppresses the diffusional decomposition reaction to form two-phase (an α phase and a Nb-enriched γ phase) cellular microstructures, which are undesirable for engineering applications.

It has been reported that the water-quenched (WQ) U6Nb alloy containing extensively twinned α'' martensitic microstructure results in low yield strength (~200 MPa) and high tensile ductility (~30%) [2]. It has also been demonstrated that the U-Nb alloy containing α'' martensite reveals sound shape memory effect [3], and the shape memory behavior is controlled mainly by the twin structures within the alloy [4]. Aging of the α'' martensite in the 150°C to 400°C range results in increase of yield strength to as high as 1.3 GPa due to very fine scale microstructural changes [5], which have not yet been fully characterized but may have been involved in spinodal decomposition. Over-aging occurs at temperatures above 400°C, where cellular decomposition occurs to form coarse two-phase cellular microstructures. The occurrence of these decompositions in association of Nb segregation can subsequently deteriorate and embrittle the alloys by reducing ductility and toughness as well as corrosion resistance [2,5]. Therefore, it is necessary to investigate and understand the aging effects on the microstructural and phase stability of WQ-U6Nb alloy. The investigation of aging effects on WQ-U6Nb reported in open literature up to present has mainly been placed on aging at temperatures above 400°C. A crucial investigation of segregation reaction within isothermally aged WQ-U6Nb below 400°C using Atom Probe Field Ion Microscopy (APFIM) has been reported in [6], where a nanometer length-scale of segregation reaction, possibly spinodal decomposition, was detected within the alloy sample aged at 300°C. Since relatively little is known about the aging mechanism of WQ-U6Nb below 400°C, our investigation was accordingly focused on the microstructure and phase stability of the alloy during isothermally aging below 200°C. Here, we reported the TEM results of modulated structure resulted from presumably spinodal decomposition within artificially aged samples as well as an important finding of the occurrence of chemical ordering within naturally aged sample.

EXPERIMENTAL DETAILS

The U6Nb alloy used for this investigation was wrought processed from Rocky Flats VAR VAR ingot at the Union Carbide Y-12 plant. Detailed information regarding the fabrication process can be found in [2]. Nb contents (in wt%) analyzed from different locations of the ingot were 5.79 (bottom edge), 5.97 (top edge), 6.03 (bottom center), and 6.10 (Top center). Five rod-shape samples of 3 mm in diameter were machined from a wrought-processed 38 mm thick plate. Each of these five samples was then encapsulated in a Cu tube and was solution treated at 800°C for 4 hours followed by water quench. One of the water-quenched samples was examined and characterized under as water-quenched condition (designated as WQ). The remaining four of the water-quenched samples were artificially aged at 200°C for 2 hours (designated as 2h), 4 hours (4h), 8 hours (8h), and 16 hours (16h). Sample NA was designated to a naturally aged sample obtained from a 15-year old stockpile. X-ray diffraction analysis was conducted to all these samples using a Philips XRG diffractometer with Cu ($K\alpha$) radiation ($\lambda = 1.5406\text{\AA}$). The employed scanning angles (2θ) for diffraction ranged from 20° to 80° with a scanning rate of 2° min^{-1} . Microhardness measurements were performed on all these samples using a Vickers-hardness indenter. The applied load was 50 g and the time duration is 35 sec for each test. To obtain a statistically significant value, six tests were conducted for each measurement. Microstructures of the WQ, the artificially aged, and the NA samples were examined using a JEOL 200CX transmission electron microscope (TEM). TEM foils were machined from the rod-shape samples and the final thinning of the foils was prepared by twinjet electropolishing in a solution of 45 vol% methanol, 45 vol% butyl alcohol and 10 vol% nitric acid at 50 V and -20°C .

DISCUSSION

Artificial aging at 200°C

Figure 1 shows the results obtained from the hardness measurement, XRD analysis, and TEM observation of WQ and artificially aged (2h, 4h, 8h, and 16 h) samples. A significant change in hardness is obtained from the artificially aged samples, which can be readily seen in Fig. 1(a). The hardness initially increases from $\text{HV } 190.0 \pm 5.8$ for the WQ sample to $\text{HV } 237.0 \pm 6.4$ and $\text{HV } 254.8 \pm 12.2$ for the 4h and 8h samples respectively and then decreases to $\text{HV } 237.3 \pm 10.0$ for the 16h sample. The age hardening/softening phenomenon observed in Fig. 1 cannot be satisfactorily interpreted by any major or significant change of phase content and microstructural morphology caused by long-range diffusion. As can be seen from the XRD and TEM results shown in Figs. 1(b) and 1(c), both WQ and artificially aged samples contain mainly the heavily twinned α'' phase, and the morphological change is insignificant. However, the hardening/softening phenomenon can be well interpreted by the occurrence of spinodal decomposition resulted from short-range diffusion, which leads to the formation of a modulated structure shown in Figs. 2(a) – 2(d). It is noted that the spinodal decomposition is a continuous clustering mechanism in which the supersaturated solid solution separates spontaneously into solute-lean and solute-rich phases within the parent phase domain through uphill diffusion, which is quite different from the nucleation and growth mechanisms via downhill diffusion [7]. It is also noted that the fine-scale modulated structure caused by spinodal decomposition generally appeared as dark/bright fringes in TEM image accompanied by the appearance of satellite (or side) spots around the Bragg spots of the diffraction pattern [8,9]. A modulated structure, which presumably contains very fine domains (~ 3 nm in size) of Nb-lean and Nb-rich phases resulted from spinodal decomposition, was first observed at a local region within the 2h sample [Fig. 3(a)]. It became more pronounced and to cover a larger portion of the 4h and 8h sample [Figs. 3(b) and (c)], which causes the hardness to increase to a maximum. Further aging causes the coarsening of the modulated structure to occur, which subsequently leads to a decrease in hardness. As can be clearly seen in Fig. 3(c), an increase of domain width to ~ 45 nm was observed within the 16h sample. Since the change of segregated phase-domains can affect the mobility of dislocation motion during deformation, it influences the hardness (strength) of artificially aged samples.

In summary, we have so far revealed an insignificant change in the phase content and microstructural morphology of alloy samples artificially aged at 200°C but detected the formation of nano-scale modulated structure within the alloy samples. The forming and coarsening of modulated domains result in the occurrence of age hardening/softening phenomenon according to the microhardness measurement. Previous work has shown significant changes in mechanical

properties as a result of the composition modulations produced by spinodal decomposition [6, 9,10]. Also, preliminary calculations suggest that the occurrence of this process is reasonable at the temperatures of the aging treatment.

Natural aging at ambient temperature

Similar to the results obtained from artificially aged samples shown above, no significant change on microstructural morphology was observed within the NA sample, which contains mainly the heavily twinned α'' phase. However, a very interesting finding made from the 15-year NA sample is the observation of swirl-shape antiphase domain boundaries (APB's) as shown in a bright-field TEM image [Figs. 3 (a)] and in a dark-field TEM image [Fig. 3(b)]. It is noted that antiphase domain boundary is also named π boundary [11] since it can only be visible when the phase angle $\alpha = 2\pi\mathbf{g}\cdot\mathbf{P} = n\pi$ (where, \mathbf{g} is the reflection vector for imaging, \mathbf{P} is the displacement vector of APB, and $n = \text{odd integers}$). The observation of APB's reveals the occurrence of disorder-order transformation, which results in the formation of chemically ordered domains within the NA sample. In essence the ordered phase domain has the same crystal structure as that of the disordered phase domain as illustrated in Fig. 4(a), except it takes up a superlattice arrangement because of the periodic occupation of lattice sites by specific atom species. The systematic variations in the atomic positions result in different order domains separated by APB's across which the atoms have wrong immediate neighbors as illustrated in Fig. 4 (b). A possible superlattice structure of a partially ordered α'' phase based on U-14at% (-6wt%) Nb is accordingly proposed according to the comparison between the observed and simulated diffraction patterns shown in Fig. 5. During the disorder-order transformation, U atoms start to occupy the following three specific lattice sites of the ordered superlattice (4 lattice sites/unit cell): $(0,5/6,1/2)$, $(1/2,1/3,1/2)$, and $(1/2,1/2,0)$, whereas 56% of the $(0,0,0)$ lattice site is occupied by Nb and 44% of the lattice site is occupied by U. Notice that the arrowed diffraction spots are superlattice diffraction, and the $[312]$ -zone diffraction pattern includes the diffraction spots generated from twin domains. Further study is needed in order to understand the disorder-order transformation within the naturally aged U6Nb.

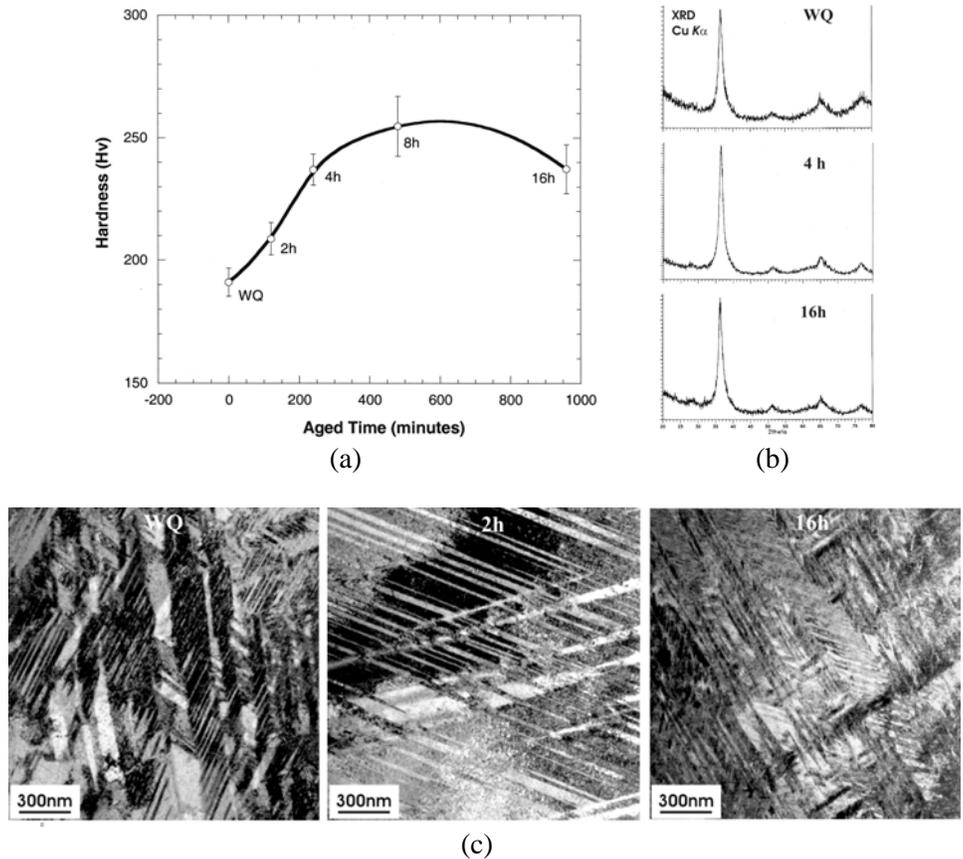


Fig. 1. Results of microhardness measurement, XRD analysis, and TEM characterization obtained from water-quenched and artificially aged alloy samples.

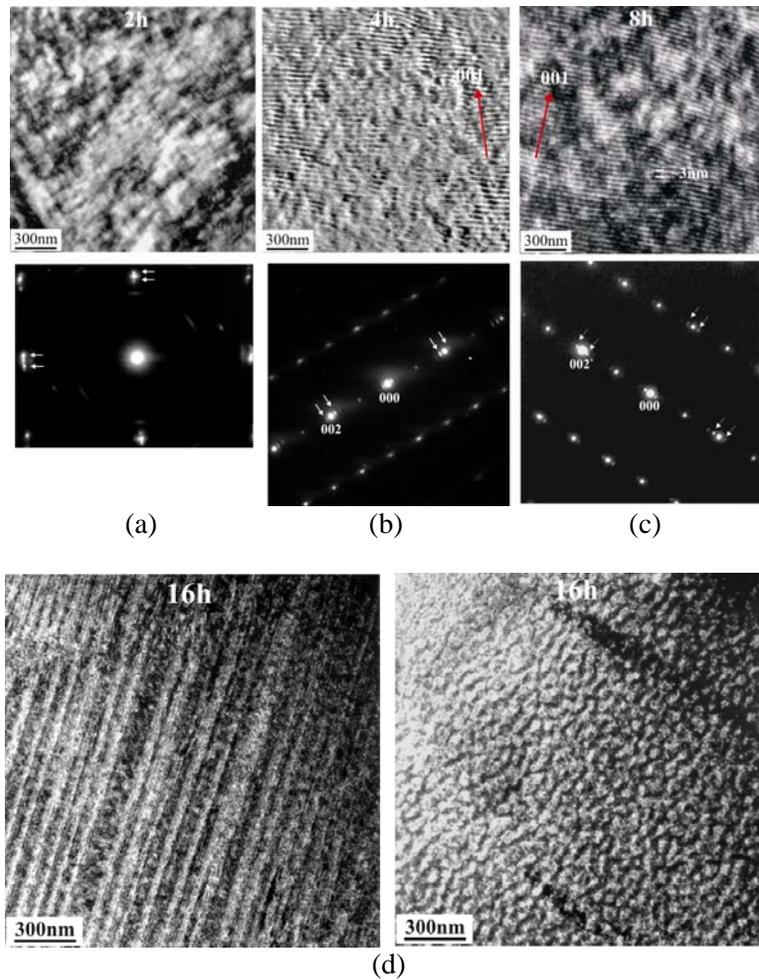


Fig. 2. TEM images and selected-area diffraction (SAD) patterns showing the formation of modulated structures within the artificially aged 2h, 4h, 8h and 16h samples. Satellite (Side) spots caused by the modulation are arrowed in SAD patterns shown in (a), (b), and (c). Coarsening of the modulation observed in 16h sample is shown in (d).

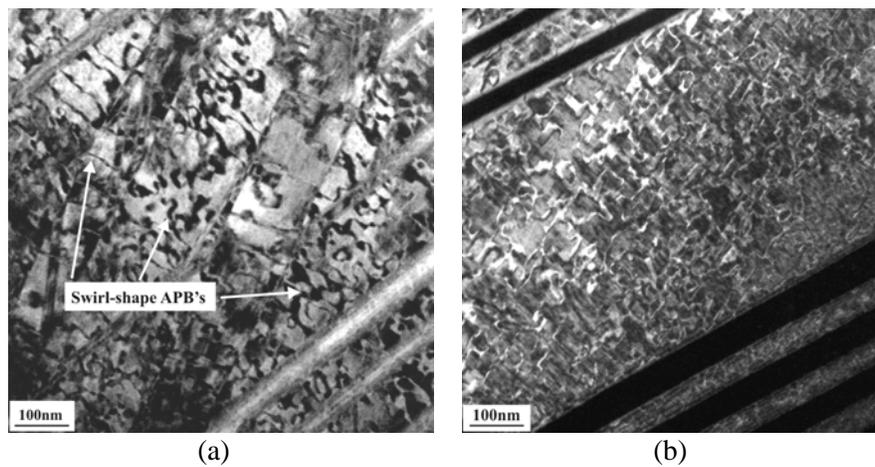


Fig. 3. Bright-field (a) and dark-field (b) TEM images reveal the formation of swirl-shape antiphase domain boundaries (APB's) within the 15-year NA sample. Notice that APB's appear as a dark contrast in (a) and a bright contrast in (b).

CONCLUSION

Aging behavior and phase stability of a water-quenched U6Nb alloy artificially aged at 200°C for different periods of time (2, 4, 8, and 16 hours) and naturally aged at ambient temperature for 15 years have been investigated. Age hardening/softening phenomenon is observed from the artificially aged samples. The hardness of the artificially aged alloy samples initially increases from HV 190.0 ± 5.8 (WQ) to HV 254.8 ± 12.2 (8h) and subsequently decreases to HV 237.3 ± 10.0 (16h). The hardening/softening phenomenon can be well rationalized by the occurrence of spinodal decomposition (i.e. the fine-scale of Nb segregation) within the artificially aged samples. A modulated structure (presumably containing very fine domains of Nb-lean and Nb-rich phases) is first found within α'' (monoclinic) parent phase at a very local region of the sample aged for 2 hours. The wavelength of the modulation (~3 nm) is determined according to the spacing of satellite spots exited by the [001] modulation around the Bragg peaks. The modulation becomes more pronounced after aging for 8 hours, which results in the increase of hardness to a maximum. Further aging of the alloy causes the coarsening of segregated domains and results in the decrease in hardness. The occurrence of order-disorder transformation is found within the naturally aged sample based upon the observation of antiphase boundaries (APB's). A new chemically ordered α'' phase is proposed based upon the comparison between observed and simulated diffraction patterns.

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