Tensile Behavior and Cold Workability of Ti-Mo Alloys

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Three kinds of titanium-molybdenum alloy, Ti-8Mo, Ti-14Mo and Ti-20Mo (mass%), quenched from 1223 K were investigated to clarify the tensile behavior and the cold workability using tensile test and conical cup test. In the quenched state Ti-14Mo showed the superior workability. Ti-20Mo has poor ductility in tensile test, but has relatively good formability in conical cup test. Both Ti-8Mo and Ti-14Mo became brittle through a cold rolling of 50% reduction in thickness; however Ti-20Mo did not change in workability by the cold rolling at all. Hardness remarkably increased with rolling reduction in Ti-8Mo and Ti-14Mo, but was almost constant in Ti-20Mo, especially with Ti-20Mo containing high oxygen. Microstructure of Ti-8Mo and Ti-14Mo rolled until seventy-odd percentage exhibited very fine structure and changed to $\alpha' + \beta$ and β structure, respectively. On the other hand Ti-20Mo hardly changed in microstructure by a cold rolling besides the formation of some band-like products. The product was composed of single variant of commensurate ω -phase, whereas the matrix contained four variants of incommensurate ω -phase. It was suggested that the peculiar deformation mechanism of Ti-20Mo was concerned with stress induced transformation of the ω -phase.

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1. Introduction

Metastable β titanium alloys are interesting in deformation properties, such as extraordinary elasticity,^{1,2)} various deformation mode,³⁻⁵⁾ shape memory effect⁶⁾ and marvelous clayey plasticity;⁷⁾ therefore they are now recognized as advanced materials for biomedical applications,^{8,9)} etc. These properties are concerned with the inherent transformations including α' -, α'' -martensites and ω -phase athermally formed by quench of the alloys.

The α' martensite with an hcp structure is formed in the alloys that contain less β stabilizers, *e.g.* Ti-6Mo,¹⁰⁾ and the α'' with an orthorhombic unit cell is formed in the alloy with a little higher content of them, *e.g.* Ti-8Mo.¹¹⁾ The difference in structure between them can be expressed by the axis ratio of b/a using an orthorhombic unit, namely that the α' takes a value 1.73 and the α'' deviates from the value. However it is difficult to draw a distinct composition boundary line between them.

The ω that is thermally formed due to an aging treatment has been well known as a cause of remarkable brittleness,^{3,4)} but the athermal ω does not show the nature in the least.⁵⁾ The athermal ω has been classified into two types according to the appearance of ω reflections in the electron diffraction pattern;¹²⁾ the ω is called "commensurate ω_c " when the ratio of $d_{0002\omega}^*/d_{222\beta}^*$ in the reciprocal space is approximately 0.663 as is found in Ti-14Mo, and "incommensurate ω_{inc} " when it is less than the value as is found in Ti-20Mo. Though the ω phase has four variants, which are uniformly distributed in the β crystal in general, certain stress conditions can give rise to deviation of the variants distribution.¹²⁾

Although many microstructural things have been investigated, the study on the plastic formability of the β titanium alloys has never been completed. It is considered as a primary reason why the industrial products made with the β titanium alloy have not appeared on the market because of high

production cost. Gum Metal™ (Ti-23Nb-0.7Ta-2Zr-O mol%) recently developed by Saito *et al.*⁷⁾ may be epoch-making material which is possible to settle this problem. If the material is cold rolling workable without limitation due to work hardening, the production cost must be drastically reduced. The purpose of this paper is to investigate the cold workability and deformation structure of typical Ti-Mo alloys.

2. Experimental Procedures

Three Ti-Mo alloys, containing 8, 14 and 20 mass% molybdenum, were prepared by a plasma arc-melting under a vacuum. They were rolled at 1223 K to 2 mm in thickness, then annealed at 1223 K for 300 s and quenched in water. After removal of an oxide scale they were cold rolled to sheets of 1 mm in thickness. These sheets had about 0.03 mass% oxygen content. Samples of tensile test, conical cup test and hardness test were cut from the sheets by a wire electric discharge machine. These samples were mechanically polished and heated at 1223 K for 900 s under a vacuum of 1×10^{-4} Pa, then quenched into iced water. Subsequently all samples were mechanically polished. The tensile test specimen was 10 mm long and 3 mm wide in the gage. Tensile test was carried out at initial strain rate of $8.33 \times 10^{-4} \text{ s}^{-1}$ until fracture. Formability was investigated by a conical cup test using 13-type jig with circular plate specimen of 36 mm in diameter and 1 mm in thickness. Vickers hardness test was used for the purpose of investigation on work hardening effect with cold rolling. Deformation microstructure was examined by Topcon EM-002B TEM with high angle tilt mode operated at 200 kV. The thin foil samples for TEM observation were prepared by electrolytic polishing using the solution consisting of methanol, n-butanol and perchloric acid. The XRD profiles were obtained to examine the structure of the quenched alloys using CuK α radiation generated at 40 kV–200 mA.

Fig. 1 Structural characteristic of quenched Ti-Mo alloys.

3. Results

Figure 1 shows XRD profiles and TEM images of three alloys quenched from 1223 K. The α'' martensites were formed in Ti-8Mo and distributed densely over the whole specimen as shown in the TEM image. In the XRD profile of Ti-14Mo the ω phase could be slightly seen besides the β phase, and it was confirmed to be the ω_c by the selected area diffraction pattern (SADP). In Ti-20Mo, though the ω phase was invisible in the XRD, it could be detected as the ω_{inc} in the SADP.

Figure 2 shows the nominal stress-strain curves of the alloys in tension at room temperature. The curve of Ti-8Mo, compared with the others, exhibited considerably gentle slope in elastic region and outstanding work-hardening after the yield. Ti-14Mo showed the low yield stress, followed by good work-hardening resulting in the excellent ductility. On the other hand Ti-20Mo showed high yield strength and low ductility without work-hardening in contrast with that of Ti-14Mo. Each elastic modulus carefully measured using a strain gauge, approximately equal to 100 GPa, was described in Table 1. Especially, that of Ti-8Mo changed gradually to lower from a quite few strain, and reached to 39 GPa beyond the strain about 0.05%; therefore the slope of the stress-strain curve was apparently lower than the others.

Fig. 2 Stress-strain curves of Ti-Mo alloys quenched from 1223 K.

Table 1 Elastic moduli of three alloys quenched from 1223 K.

Alloy	Ti-8Mo	Ti-14Mo	Ti-20Mo
Elastic modulus, E /GPa	95 (ϵ : $\sim 0.05\%$) ↓ 39 (ϵ : $0.05\% \sim$)	104	91

Figure 3 shows the optical micrographs of deformation structure after fracture in tension. Many needle-like martensites which had not been observed before deformation were visible on the surface of Ti-8Mo; neither slip lines nor twin bands could be recognized. Peculiar $\{332\}\langle 113 \rangle$ twins were observed in Ti-14Mo, and coarse slip lines in Ti-20Mo.

Figure 4 shows the result of the conical cup test on the quenched alloys; load vs. punch displacement curves, the whole shapes and the head appearances of the cups. As expected from the stress-strain curve, the excellent formability was proved on Ti-14Mo, and unexpectedly Ti-20Mo exhibited relatively good formability. The head surface of all the cups showed an orange peel.

Figure 5 also shows the result of the conical cup test on the alloys which were cold-rolled to the thickness of 1 mm from 2 mm after quench. The specimen of Ti-8Mo had no formability owing to the extreme work-hardening during cold rolling, and fractured into halves at the initial stage. Ti-14Mo was also degraded on formability, requiring a load two times as large as the quenched specimen at 10 mm punch stroke. On the other hand Ti-20Mo kept good formability; the behavior of the rolled specimen was similar to the quenched one in every respect.

Change of Vickers hardness with cold rolling on the three alloys was measured to examine the effect of work-hardening as shown in Fig. 6. The hardness of the quenched alloys indicated an increase with the Mo content. Both Ti-8Mo and Ti-14Mo exhibited typical work-hardening in proportion to the roll reduction. Ti-20Mo was hardened by the first rolling, but hardly showed the work-hardening with subsequent

Fig. 3 Optical microstructure of Ti-Mo alloys deformed in tension.

Fig. 4 Load vs. punch displacement curves and appearance of quenched samples by conical cup test.

rolling. As compared with that, the result of Ti-20Mo containing higher oxygen about 0.36 mass% was also drawn in this figure. Though considerably raised before rolling by the interstitials of oxygen, the hardness was not changed with rolling at all.

TEM observation was carried out on the three low oxygen alloys rolled until seventy-odd percentage. Figure 7 shows

TEM image and SADP of the rolled Ti-8Mo. There was very fine structure with no sign of the α'' martensites due to the severe cold rolling; the SADP exhibited the ring pattern which were assigned to α' and β phases, but not to α'' martensite. Figure 8 shows the rolled Ti-14Mo in the same manner. Though the microstructure was similar to that of the rolled Ti-8Mo, it was composed of single β phase without ω phase. On the contrary the microstructure of the rolled Ti-20Mo was quite different from the others as shown in Fig. 9.

Fig. 6 Hardness change with cold rolling of Ti-Mo alloys quenched from 1223 K.

Fig. 8 Microstructure and SADP of Ti-14Mo alloy rolled up to 70%.

like products were detected in places as shown in Fig. 9. The inserted SADPs taken from the matrix and the product indicated the same (111) pattern of the β phase. For the purpose of investigating the structural difference between them, several SADPs from the same positions were taken by tilting the TEM specimen. Figure 10 shows the SADPs from the various orientations, (101), (113), (111) and (110), denoted by large solid circles in the stereo projection. Though (101) patterns from the matrix and the product were indicating basically the same diffuse scattering of the ω_{inc} , the patterns of (113) and (110) were different between the matrix and the product in the appearance of the ω phase scattering; that is, the ω phase was varied in the product to the single variant of ω_c phase.

4. Discussion

4.1 Ti-8Mo

The apparent elastic slope of the stress-strain curve on Ti-8Mo in Fig. 2 is considerably lower than the others, suggesting the occurrence of stress induced martensite (SIM) transformation during the test. The SIM transformation, as reported by some researchers,¹³⁾ must be easy to occur, since the b/a ratio of the α'' in Ti-8Mo about 1.65 in the present work, is relatively close to 1.73 of the α' , and the composition boundary of α'/α'' formation has been regarded

Any refined structure such as Figs. 7 and 8 was not discovered although the TEM observation was extensively carried out, and the SADPs obtained from anywhere showed sharp diffraction spots without streaking. Instead some band-

Fig. 9 Microstructure and SADP of Ti-20Mo alloy rolled up to 70%.

as Ti-6Mo approximately.¹⁰⁾ Therefore it is considered that the volume expansion with the $\alpha'' \rightarrow \alpha'$ SIM transformation during the test causes apparent low elastic slope. Actually a certain pseudo elastic effect was confirmed through the cyclic tensile test of Ti-8Mo, although the response of the inverse transformation with a stress release was not so sensitive. If improved in sensitivity to the response, such an alloy with low elastic slope is available for a biomaterial.

4.2 Ti-14Mo

As for quenched Ti-Mo alloys Ti-14Mo exhibited prominent ductility and formability due to the $\{332\}\langle 113 \rangle$ twin formation. It is well known that the athermal ω_c formed by quenching is one of the conditions for the $\{332\}\langle 113 \rangle$ twin formation,¹²⁾ though it is not clear how the ω_c is concerned with the formation. The $\{332\}\langle 113 \rangle$ twinning requires only half the shear strain required for $\{112\}\langle 111 \rangle$ twin, and its formation is related to the α'' martensite transformation at the interface between the matrix and the twin;⁵⁾ therefore Ti-14Mo has good ductility in spite of twin mode.

4.3 Ti-20Mo

Ti-20Mo is very interesting with respect to its workability just like a clay material, where mechanical properties remain unchanged by cold rolling. It should be noted that the structure of the heavily rolled specimen hardly changed

besides the formation of the band-like products composed of single variant of the ω_c phase. It is reasonable that the similarity on the structure before and after cold rolling means the equivalency of the mechanical properties, and that the deformation is undertaken only at the band-like product.

We can describe the deformation mechanism of Ti-20Mo as shown in Fig. 11. The ω_{inc} phase of the quenched specimen is expected to turn into the ω_c phase with a stress increase,¹⁴⁾ and as a result uniform distribution of the ω_c phase variants leads to a rise of the yield stress. However when the stress becomes high than a certain level in the stress-concentrated area such as around a crack, the ω_c variants but a specific one would disappear, and then single ω_c variant band would be formed toward the direction of a stress-concentration. The specific variant left in the band product must be deformable to the stress, resulting in occurrence of the concentrated slip at the band. Since the band product, scattered in the crystal, is able to undertake a large quantity of deformation, it is not expected to act on the work-hardening. When the specimen is unloaded after deformation, the ω_c phase will return to the ω_{inc} phase as before, and the band product will become a bundle of dislocations.

However, good ductility in the conical cup test means that the work-hardening arose at least in the parietal of the cup. An equi-biaxial tensile condition generated in the parietal part would be expected to yield the band-like products in several directions. Some band products would collide each other and it is considered that the deformation in the part may become difficult as a result.

Poor work-hardening phenomenon in the cold-rolling of Ti-20Mo is very similar to that of the Gum metal, which is also outstanding in a higher oxygen alloy.⁷⁾ It is known that oxygen is an element of α stabilizer in general and has an effect to suppress the formation of ω phase.¹⁵⁾ As for the mechanical properties, oxygen considerably raises the yield stress and tends to decrease the work-hardening rate. Probably a small number of the band products are generated in a higher oxygen alloy, but the deformation may be extremely concentrated in the band products resulting in the non work-hardening.

5. Conclusions

Tensile behavior and cold workability of three kinds of Ti-Mo alloys were investigated from the standpoint of microstructure, and the characteristics of each alloy can be summarized as follows:

(1) Ti-8Mo showed an apparent low elastic slope of the stress-strain curve corresponding to the $\alpha'' \rightarrow \alpha'$ SIM transformation. The α'' martensite changed to the very fine structure of $\alpha' + \beta$ phases by heavy cold rolling.

(2) Ti-14Mo exhibited prominent ductility and formability due to the $\{332\}\langle 113 \rangle$ twin formation; however it was degraded on formability by cold rolling.

(3) Workability of Ti-20Mo was not changed before and after cold rolling at all. Moreover microstructure was also hardly changed besides the formation of the band-like products composed of single variant of the ω_c phase. It is suggested that the band product is possible to deform within the band resulting in the non work hardening.

Fig. 10 SADPs of the product and the matrix with tilting of the specimen.

Fig. 11 Schematic illustration of structural change of ω phase in Ti-20Mo alloy with tensile-stress increase.

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