Elastic Deformation Behavior of Multi-Functional Ti–Nb–Ta–Zr–O Alloys

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We investigated the effect of cold working on the elastic properties of a newly developed multi-functional β titanium alloy, GUM METAL, using in-situ XRD and EBSD analysis. Mechanical and physical properties are changed dramatically by cold working. The alloy has a low elastic modulus (40 GPa), high strength (more than 1100 MPa), high elastic deformability (2.5%) and super-plastic like deformability at room temperature without work hardening. The elastic behavior of the cold worked specimen shows non-linearity, with the gradient of the stress-strain curve in the elastic region continuously decreasing with a stress increase. In-situ XRD measurements during tensile loading show that all β peaks shift monotonically to higher 2θ angles with increasing tensile strain up to 2.7%. This result suggests that the elastic behavior in the alloy is not accompanied by phase transformations, such as stress-induced α’'. Additionally, EBSD analysis reveals that the deformation mode in the alloy does not relate to {112} and (332) twinning. The microstructure of the alloy during deformation is characterized by localized distorted regions ranging in size from several tens of micrometers to submicrometers, with elastic strain located hierarchically in the alloy. It is likely that this microstructure is attributable to its elastic anomaly, which arises at this specific alloy composition of the multifunctional alloy. The above elastic anomaly in the alloy seems to contribute to the development of the unique microstructure during plastic deformation, as well as to its macroscopic elastic behavior.

1. Introduction

It is well known that the elastic modulus of titanium is reduced by the addition of Va group elements such as niobium, tantalum and vanadium. Due to these experimental results, much effort has been made to develop new titanium alloys having a low elastic modulus with high strength, especially for use in artificial bone or implants. However, none of these alloys were completely satisfactory. Moreover, there have been few attempts to theoretically compute and predict elastic moduli of titanium-based alloys.

We have recently developed a new β titanium alloy, GUM METAL, which exhibits a low elastic modulus with high strength, by using a new alloy design method that uses theoretical calculation. This new theoretical calculation, which is based on the ultra-soft pseudo-potential method within a generalized gradient approximation to the density function theory, can accurately predict the elastic modulus by calculating elastic constants \(c_{11}, c_{12}, c_{44}\) of Ti–X binary alloys \((X = V, Nb, Ta, Mo and W)\). From the calculation results, we found that \(c_{11} - c_{12}\) is correlated with the averaged valence electron number \(e/a\). In Ti–25 at%Nb, whose \(e/a\) is 4.25, the elastic anisotropy is significant and the elastic modulus in \(001\) and the shear moduli along \(011\) on \(011\) and along \(111\) on \{011\}, \{112\} or \{123\} show a very small value. This coincides with the result that the value \((c_{11} - c_{12})\) approaches zero when \(e/a\) is close to 4.24. The results also indicated that the polycrystalline elastic modulus of Ti–X binary alloys, which is calculated from the elastic constants of the single crystal by the Voigt–Reuss–Hill method, reaches a minimum value at \(e/a\) of around 4.24. As a result, we believe that an \(e/a\) of around 4.24 is one of the most important requirements for designing a low elastic modulus titanium alloy. Next, we experimentally investigated the group IVa elements, which improve the strength of the alloy without increasing the elastic modulus, by changing the combination of the bond order \(Bo\) and the “d” electron-orbital energy level \(Md\) value based on the DV-Xα method, while maintaining an \(e/a\) value of 4.24. We determined the optimum combination of the three electronic numbers to be: an \(e/a\) of around 4.24; a \(Bo\) of around 2.87; and an \(Md\) of around 2.45. The unique properties such as low elastic modulus, high strength and superior cold-workability only appear when all three of these magic numbers are satisfied simultaneously, and each alloy system requires significant cold working and the presence of at least 0.7% oxygen. The composition of the developed alloy is fundamentally expressed as Ti–24 at% (Ta + Nb + V)–(Zr, Hf)–O. Various alloy compositions are available, such as Ti–23Nb–0.7Ta–2Zr–O alloy and Ti–12Ta–9Nb–3V–3Zr–O alloy (in at%), where each alloy has a simple body-centered-cubic (bcc) crystal structure.

In the present paper, we first evaluated quantitatively the effect of cold working on the elastic properties of the Ti–23Nb–0.7Ta–2Zr–6O–1.2O alloy. We also carried out experimental verification of the bcc phase stability during elastic deformation and a detailed observation of the microstructure after plastic deformation. Finally, we discuss possible relationships between the characteristic microstructure of the alloy and its elastic properties in which strong anisotropy can be expected to occur.

2. Experimental

We used mainly Ti–23Nb–0.7Ta–2Zr–1.2O alloy to examine the detailed elastic behavior of the multifunctional alloy. We also used Ti–21Nb–0.7Ta–2Zr–1.2O alloy and Ti–25Nb–0.7Ta–2Zr–1.2O alloy to study the bcc stability. Pure titanium powder and other powders for alloying, such as titanium, niobium, tantalum and zirconium, were blended at predetermined compositions in a rotation mill for 7.2 ks. The mixed powder was compacted into a cylindrical shape by
cold isostatic pressing (CIP’ing) at a pressure of 392 MPa, sintered at 1573 K for 14.4 ks in a vacuum of $10^{-3}$ Pa, and cooled in the furnace to room temperature. The sintered billet was hot forged at 1423 K and subsequently formed into a round bar. The surface oxidized layer was peeled off the bar, and the bar was then solution treated at 1273 K for 3.6 ks in an argon atmosphere, quenched in water, and then cold worked in a rotary swaging machine. The oxygen content of the material was controlled by mixing in a titanium powder with a high oxygen content (3.0 at% O).

Tensile tests were carried out on smooth cylindrical specimens 2 mm in diameter with a 10 mm gauge length at a strain rate of $5 \times 10^{-4}$ s$^{-1}$ at room temperature. Tensile strain was measured by the strain gauge method to enable an accurate evaluation of the elastic modulus and the attainable elastic strain before plastic deformation. Two strain gauges were attached to the parallel portion of the specimen surface. The elastic limit strength was determined experimentally from stress–strain curve. We defined a maximum strength in the stress–strain relation with no hysteresis as the elastic limit strength. Work hardening behavior was examined by the Vickers hardness test at a load of 49 N.

Microstructural characterization was conducted using a combination of optical microscopy (OM), electron backscatter diffraction patterns (EBSP), transmission electron microscopy (TEM), and X-ray diffraction (XRD). All specimens were prepared in the section vertical to the swaging direction. Polished specimens for OM were prepared by a conventional mechanical technique and were etched with an aqueous 10% HF + 10% HNO$_3$ solution. Specimens for EBSP and XRD were prepared by electro polishing and chemical polishing, respectively. EBSP measurements were carried out using an X-ray diffractometer with Cu-K$_\alpha$ radiation at a scanning speed of 0.04$^\circ$/s. A thin film for TEM was cut into a small disk 0.5 mm thick, mechanically polished to 0.15 mm thick and electrolytically polished by the twin-jet method at 10 V. Observation was made by TEM with an acceleration voltage of 200 keV.

3. Results

Figure 1 shows the change in the tensile stress–strain curve at room temperature with 90% cold working for the Ti–23Nb–0.7Ta–2Zr–1.2O alloy. The elastic modulus is dramatically dropped by the cold working from 70 to 55 GPa at near zero stress and the yield stress increases after cold working. We can confirm non-linearity in elasticity for the cold worked specimen, with the gradient of the stress–strain curve in the elastic region continuously decreasing with the stress increase. As a result of the decrease in the modulus and its non-linearity, the elastic deformability after cold working reached 2.5%, which is at least double that before cold working. Figure 2 shows changes in tensile properties with cold working ratio. The elastic limit strength of the solution treatment material is about 750 MPa. After 20% cold working, the strength reaches 900 MPa. Subsequently, it gradually increases with increasing cold working, attaining 1050 MPa after 90% cold working. The elongation decreases to about 10 after 20% cold working, but then remains approximately constant until 90% cold working.

Figure 3 shows changes in elastic properties, such as the initial and average elastic moduli and the attainable elastic strain, with cold working. Here, the initial elastic modulus is the gradient of the stress–strain curve at near zero stress and the average one is the average value of the gradients during elastic deformation with the non-linearity. The attainable elastic strain of the solution treatment material is about 1% and increases to 2.5% after 90% cold working. Both elastic moduli decrease with increasing cold working ratio, particularly, the downward trend in average elastic modulus is preeminent and decreases to below 40 GPa at 90% cold working. Figure 4 shows effects of cold working on hardness and reduction in area. The Vickers hardness and the reduction in area of the alloy both remain approximately constant regardless of the cold working ratio. On the other hand, the

![Fig. 1 Change in tensile stress–strain curve at room temperature with 90% cold working.](image1)

![Fig. 2 Changes in elastic limit strength and elongation with cold working ratio.](image2)
hardness of the conventional $\beta$ titanium alloy gradually increases with an increasing cold working ratio. This suggests that the multifunctional alloy has super-plastic like deformability at room temperature without work hardening.\(^{5,6}\) Since the alloy does not show work hardening after cold working, continuous deformation without annealing is possible to more than 99.9\% under any kind of cold working, such as formation of a round bar, wire or thin sheet.

Optical micrographs of Ti–23Nb–0.7Ta–2Zr–1.2O alloy (Fig. 5) show that the microstructure changes dramatically during cold working. The microstructure in Fig. 5(a) (before cold working) is composed of equiaxed grains 50 to 100 $\mu m$ in size. Lenticular deformation bands are observed to appear in the coarse equiaxed grain after 40\% cold working [Fig. 5(b)]. Subsequently, as the cold working ratio increases, the deformation bands are gradually distorted as seen in
Fig. 5(c), and after 90% cold working, the microstructure finally changes into a characteristic “marble-like” structure [Fig. 5(d)]. The marble-like microstructure is composed of assemblies of fine filamentary structure. Although the microstructure changes dramatically as seen in Fig. 5, the phase configuration doesn’t change at all, even after heavy cold working. Namely, the XRD profile after cold working (Fig. 6) does not show the presence of any peaks other than the β (bcc) phase. It is also inferred from the XRD profile after cold working that the preferred orientation of (011) is formed by crystallographic rotation as the plastic working proceeds.

4. Discussion

4.1 Elastic deformation behavior and bcc phase stability

It is well known that the large elastic deformation obtained in “super-elastic alloys” originates from reversible martensitic transformation, dubbed “pseudo-elastic deformation”, in which substantial hysteresis can be seen in the stress–strain curve. Conversely, the multifunctional alloy shows a quite unique elastic behavior with no hysteresis in the stress–strain relation. Therefore, it is likely that the elastic behavior of the alloy is completely different from that of the conventional ones.

Hence, let us consider the relationship between elastic deformation behavior and bcc phase stability. Figure 7 shows the change in elastic deformation behavior effected by Nb contents in Ti–Nb–Ta–Zr–O alloys. The stress–strain curve of the lower Nb containing alloy, Ti–21Nb–0.7Ta–2Zr–1.2O alloy, indicates pseudo-elastic deformation. On the other hand, the higher Nb containing alloy, Ti–25Nb–0.7Ta–2Zr–1.2O alloy, has a linear stress–strain relationship in the elastic range as is often seen in conventional β titanium alloys. The multifunctional alloy, Ti–23Nb–0.7Ta–2Zr–1.2O alloy, has unique elastic behavior with non-linearity in the elastic range. In order to characterize crystallographic information during the elastic deformation of the alloy, in-situ XRD measurements during tensile loading were conducted using sheet specimens made from the 90% cold swaged material. Figure 8 shows in-situ measurement results representing typical reflection peaks, around {011} and {002} β, during the tensile loading for the cold worked alloys. A reflection peak of stress-induced α’ martensite is observed in the lower Nb containing alloy before tensile loading, as seen in Fig. 8(a). Along with increasing strain, the {020} α’ reflection becomes weaker while the {011} β reflection becomes stronger. This phenomenon can be interpreted by
considering the orientation relationship between $\beta$ and $\alpha''$. Namely, the orientation relationship is known as $(110)\beta // (020)\alpha''$ and $(001)\beta // (002)\alpha''$ for transformation from $\beta$ to $\alpha''$ which yields 2.4% expansion in the $(110)\beta$ direction and 2.4% compression in the $(001)\beta$ direction, respectively. Tensile loading generates compressive stress in sheet thickness. Hence, $(020)\alpha''$ on the rolling plane is compressed and retransforms to $(110)\beta$ with increasing tensile strain. In the lower Nb containing alloy, obvious rearrangement of variants of $\alpha''$ occurs, and the stress–strain curve can be explained by reversible martensitic transformation, dubbed "pseudo-elastic deformation". Figure 8(b) shows the result for the multifunctional alloy, in which each $\beta$ peak shifts monotonically to a higher $2\theta$ angle with increasing tensile strain up to 2.7%. This result suggests that no phase transformation occurs during tensile loading. In the higher Nb containing alloy, the $(011)\beta$ peak shifts monotonically with increasing tensile strain up to 1.2%, and then the peak shift stops, as seen in Fig. 8(c). Figure 9 shows the change in the lattice plane spacing estimated from the peak shift values of $(001)$ and $(112)$ $\beta$ as a function of the tensile strain in Ti–23Nb–0.7Ta–2Zr–1.2O alloy and Ti–25Nb–0.7Ta–2Zr–1.2O alloy. The lattice plane spacing of the multifunctional alloy, Ti–23Nb–0.7Ta–2Zr–1.2O alloy, continuously changes as the tensile strain increases up to 2.7%. This means that the elastic deformation continues to a tensile strain of as much as 2.7%, as shown in Fig. 1. In the case of the higher Nb containing alloy, Ti–25Nb–0.7Ta–2Zr–1.2O alloy, the change in the lattice plane spacing is saturated at 1.2% tensile strain, which suggests that plastic deformation occurs at more than 1.2% tensile strain. As observed above, there is no doubt about the fact that no transformation such as stress-induced $\alpha''$ or rearrangement of variants of $\alpha''$ occurs in Ti–23Nb–0.7Ta–2Zr–1.2O alloy.

### 4.2 Microstructure development during plastic deformation

The unique properties of the multifunctional alloy are achieved only after cold working, which implies that the internal constitution of the cold worked alloy plays a crucial role in the development of those properties. Deformation bands are observed in Fig. 5, and their appearance is similar to that of deformation twins. $(112)(111)$ twinning often occurs in bcc metals and alloys. In addition to this, $(332)(113)$ twinning, advocated by Cocker, has been reported to take place in metastable $\beta$ titanium alloys at room temperature, by Hanada et al. Crystallographic misorientation between matrix and twin in $(112)(111)$ or $(332)(113)$ twinning is about 70.3 or 50.5 degrees, respectively, around the $(110)$ axis. First, we carried out a detailed observation of the microstructural changes with cold working, using EBSP to investigate the internal constitution of the unique "marble like" microstructure.

Figure 10 shows an example of an inverse pole figure map obtained by EBSP for the specimen shown in Fig. 5(b); the swaging direction is normal to the measured plane. The change in color in each grain corresponds to that in crystal orientation. We can see that most of the grains are divided into sections by boundaries and/or have a continuous orientation change without clear boundaries. Figure 11 shows point-to-point misorientation across the orientation boundaries in the interior of the grains and orientation gaps between the grain-rotation axis and the $(110)$ axis. The crystallographic misorientations are less than 30 degrees and the gap between the axes is in the range between 10 and 30 degrees. Therefore, it seems reasonable to at least conclude that the boundaries shown in Fig. 5(b) are not twin boundaries. We also performed a similar analysis on a specimen that was cold swaged by 85%. Figure 12 shows an example of the crystallographic misorientations without any boundaries in the grain. The point-to-point misorientation is less than 10 degrees. This result also proves clearly that a deformation mode in the alloy does not relate to twinning. Additionally, the important point in this result is a continuous grain rotation of more than 50 degrees across a distance of about 45 μm. It is quite likely that a local area of distortion like this has a considerable amount of residual stress. Since the alloy has a very low elastic modulus, quite a lot of localized elastic strain would be accumulated in the alloy after plastic deformation.

It was inferred from the XRD analysis results that the elastic deformation mode of the multifunctional alloy is different from that of stress induced martensitic transformation. EBSP results indicated that the elastic strain was
accumulated in the cold worked microstructure. Here we will discuss the internal constitutions of such a unique microstructure. Figure 13 shows examples of the microstructure of a specimen after 90% cold working. In Figs. 13(b), (c), the electron beam was parallel to the longitudinal direction of the cold swaged bar. The microstructure shown in Fig. 13(b) is a mixture of grains several tens of micrometers to submicrometers in size. Figure 13(c) shows a magnified image of the flecked contrast. The elastic field seems to be a fractal-like microstructure, which means that the elastic field induced by cold working is located hierarchically in the alloy from micrometer to nanometer. Namely, the assemblies of fine filamentary structure seen in Fig. 13(a) correspond to a
gathering of localized elastic strain in Figs. 13(b) and (c), which is accumulated discretely and hierarchically in the alloy.

In the previous paper,\(^7\) we have shown that \((c_{11}-c_{12})\) takes a value close to zero around the composition of the multifunctional alloy, namely at an \(e/a\) value of around 4.24. When \((c_{11}-c_{12})\) approaches zero, the elastic modulus in \((001)\) and the shear moduli along \((011)\) on \((011)\) and along \((111)\) on \((011), (112)\) or \((123)\) exhibit a very small value. This suggests that the "ideal strength"\(^1\) of the alloy is extremely small. Dislocation glide occurs along \((111)\) on \((011), (112)\) or \((123)\) in conventional bcc metal when local stress reaches the critical value. In the case of the alloy, the applied stress can be relaxed by localized elastic deformation due to its extremely low shear modulus in the specific directions. It seems that such elastic relaxation can be related to plastic deformation without deformation twinning. At a certain amount of loading, a shear deformation can proceed suddenly along the maximum shear stress plane without any aid of dislocations, when the local stress is nearly equal to the ideal stress of the alloy.\(^5\) As plastic working proceeds, highly distorted and localized elastic strain is accumulated in the fine filamentary structure seen in Fig. 13. The above elastic anomaly in the multifunctional alloy seems to contribute to the development of its unique microstructure during plastic deformation, as well as to its macroscopic elastic behavior.

5. Summary

We investigated the effect of cold working on the unique elastic properties of Ti–23Nb–0.7Ta–2Zr–1.2O alloy and discussed the accumulation of elastic strain energy during plastic deformation in the alloy.

(1) The elastic modulus of the developed alloy is decreased dramatically by cold working. After 90% cold working, the alloy has a low elastic modulus (40 GPa), high strength (more than 1100 MPa), and high elastic deformability (2.5%). The alloy also has super-plastic like deformability at room temperature without work hardening.

(2) In situ XRD revealed that the elastic behavior in the developed alloy is not accompanied by phase transformations, such as stress-induced \(\alpha''\). EBSP analysis revealed that the deformation mode in the alloy does not relate to \([112][111]\) or \([332][113]\) twinning.

(3) The microstructure of the alloy during deformation is characterized by a localized distorted region ranging from several tens of micrometers to submicrometers in size, with the elastic strain being located hierarchically in the alloy. It is likely that such microstructure is attributable to its elastic anomaly, which arises at this specific alloy composition of the multifunctional alloy.

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