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Beta Ti Alloys with Low Young's Modulus

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Composition dependence of Young's modulus in β Ti-V and Ti-Nb binary alloys and Sn-added ternary alloys quenched from β phase region was investigated at room temperature in relation to the stability of β phase. A minimum of Young's modulus in the binary alloys appears at such a composition that athermal ω phase transformation is almost completely suppressed. Formation of isothermal ω phase by aging after quenching increases Young's modulus. Sn addition to the binary alloys suppresses or retards ω transformation, thereby decreasing Young's modulus. Optimization of alloy composition in Ti-Nb-Sn alloys leads to low Young's modulus of about 40 GPa. The composition dependence of Young's modulus obtained experimentally in this study can be qualitatively explained by the theoretical discrete-variational Xα cluster method.

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1. Introduction

Commercially developed α, $\alpha + \beta$ and β Ti alloys can provide a wide variety of mechanical properties such as strength, ductility and toughness by controlling alloy composition, volume fraction of constituent phases and microstructure. However, as far as Young's modulus is concerned, most of commercially available Ti alloys possess almost similar values from 80 to 110 GPa which are approximately one half that of steels. If Young's modulus of Ti alloys can be largely increased or decreased by alloy design, their industrial applications will be widely expanded. Although dispersion of hard particles such as carbide or boride is known to considerably increase Young's modulus of Ti alloys, no reliable concept necessary for designing low Young's modulus Ti alloys was established. Recently, Kuroda *et al.*[1] have developed new β Ti quaternary alloys, Ti-Nb-Ta-Zr, Ti-Nb-Ta-Mo and Ti-Nb-Ta-Sn, with low elastic modulus of about 50 GPa based on the molecular orbital calculation of electronic structures (called discrete-variational Xα cluster method, DV-Xα cluster method) proposed by Morinaga *et al.*[2] This result suggests that the theoretical method is applicable to the development of β Ti alloys with low elastic modulus.

This work aims to experimentally measure the composition dependence of Young's modulus in relation to β phase stability and to discuss the applicability of the theory described above to the development of low Young's modulus β Ti alloys, using simple β Ti-V and Ti-Nb binary alloys and Sn-added ternary alloys.

2. Experimental

Ti-V binary alloys with 10 different compositions of Ti-(16 to 50)mass%V, Ti-Nb binary alloys with 8 different compositions of Ti-(36 to 52)mass%Nb, Ti-V-Sn ternary alloys with 3 different compositions of (Ti-20 mass%V)-(2.4 to 7)mass%Sn and Ti-Nb-Sn ternary alloys with 29 different compositions of Ti-(23 to 43)mass%Nb-(5 to 15)mass%Sn were prepared by arc-melting in an argon atmosphere using high purity Ti, Nb and Sn. Since weight changes before and after the arc-melting were negligible, alloy compositions will be denoted hereafter by nominal compositions. The arc-melted buttons were cold rolled to 4 mm in thickness and homogenized in vacuum at 1423 K for 24 h. The annealed plates were again cold rolled to 1.5 mm in thickness, solution treated at 1223 K for 30 min in an evacuated quartz tube and then quenched in ice water. Microstructures were identified by X-ray diffraction (XRD), optical microscopy and transmission electron microscopy (TEM). Young's modulus was measured mainly in the rolling direction at room temperature (298 K) by the free resonance vibration method (Nihon Techno-Plus Corporation JE-RT) using a sample with dimensions 50 mm (length in the rolling direction) $\times$ 10 mm (width) $\times$ 1 mm (thickness). Young's modulus of some samples was measured in the 45° and 90° directions to the rolling direction to investigate the effect of recrystallization texture on Young's modulus. The recrystallization texture was measured by the conventional X-ray reflection method.

3. Results and Discussion

Figure 1 shows Young's modulus of as-quenched Ti-V binary alloys as a function of V content, which was reported by Knorr and Scholl[3] and Graft *et al.*[4] Young's modulus of as-quenched and aged β TiV alloys in this work is plotted in this figure. It is known that β phase at high temperatures is retained by quenching at V content higher than 16 mass%. The measured values for the as-quenched β TiV alloys in this work are in fairly good agreement with those in their works. Young's modulus of β Ti alloys exhibits a minimum at around Ti-25 mass%V. According to TEM observations,[5] athermal ω reflections as well as bcc fundamental reflections were seen in electron diffraction patterns of β Ti-V alloys, depending on alloy composition. Very fine ω particles were observed with a high density at low V contents. With increasing V content the intensities of ω reflections became weak, changed to diffuse scattering and disappeared. The minimum in Young's modulus corresponds to a composition at which diffuse scattering is observed. This result implies that Young's modulus at low V contents in the β phase region is increased by athermal ω phase.

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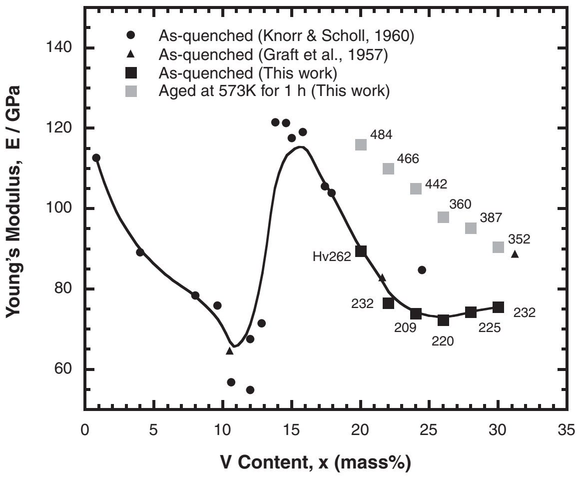

Fig. 1 V content dependence of Young's modulus in quenched Ti-V binary alloys.

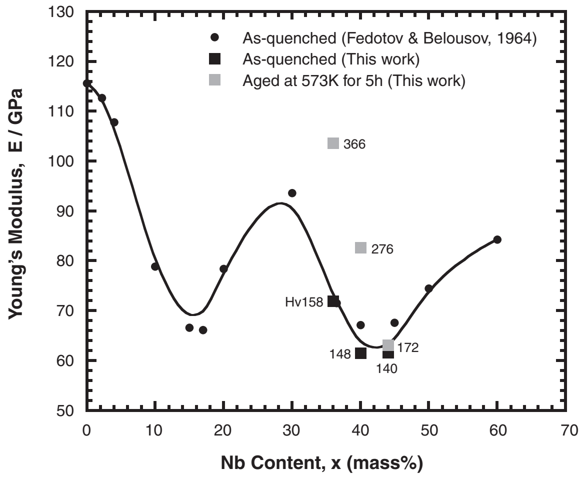

Fig. 2 Nb content dependence of Young's modulus in quenched Ti-Nb binary alloys.

It is interesting to note that with increasing V content in β Ti-V binary alloys plastic deformation mode changes from deformation twinning to crystallographic slip around a composition at which ω reflections become extremely weak.[6] This is probably because crystallographic slip is difficult in the bcc matrix containing finely distributed ω phase particles with a high density. Instead, $\{332\}\langle 113\rangle$ twinning accompanied by shuffling of half of atoms would precede slip if inhomogeneous internal stress fields created by fine ω particles could assist the shuffling.

β Ti-V binary alloys were aged at 573 K for 1 h to investigate the relation between Young's modulus and isothermal ω phase. Obtained results are included in Fig. 1. Obviously, Young's modulus of all the β Ti alloys investigated increases remarkably by aging. Vickers hardness denoted by numbers in the figure also shows that age hardening occurs significantly, *e.g.*, Vickers hardness of Ti-20 mass%V increases by aging from 262 to 484. The increase in hardness was confirmed to be due to ω precipitation by XRD and TEM. In contrast, no apparent change in hardness was observed in aged Ti-50 mass%V.

A quite similar tendency was observed in β Ti-Nb binary alloys. Figure 2 shows the composition dependence of Young's modulus for alloys quenched from the β region, which was reported by Fedotov and Belousov.[7] Young's modulus of as-quenched and aged β TiNb alloys in this work is plotted in this figure. It is known that β phase at high temperatures is retained by quenching at Nb content higher than 36 mass%. The values for the as-quenched β TiNb alloys in this work are in good agreement with those in their work. A minimum in Young's modulus is observed at around the composition of Ti-40 mass%Nb. Again, it should be noted in a similar manner to β Ti-V alloys that deformation twinning is preferentially caused at plastic yielding.[6,8] That is, according to the references, in the composition range where Young's modulus increases with decreasing Nb content, $\{332\}\langle 113\rangle$ twinning is exclusively caused by plastic deformation. Age-hardening by ω precipitation occurs pronouncedly at Ti-36 and 40 mass%Nb alloys, thereby increasing Young's modulus remarkably. No marked ω precipitation in aged Ti-42 mass%Nb was observed by XRD and TEM. Correspondingly, no significant increase is seen in Vickers hardness and Young's modulus. As can be seen in Figs. 1 and 2, a minimum composition in Young's modulus after aging moves toward higher solute content, since isothermal ω transformation, depending on alloy composition, occurs significantly even at the composition exhibiting the minimum in Young's modulus in as-quenched alloys.

The results described above demonstrate that low Young's modulus in β Ti alloys is achieved at such a composition that with increasing alloying content athermal ω is almost completely suppressed on quenching. Therefore, alloying with a ternary element suppressing ω transformation was investigated to further decrease Young's modulus. It has been reported that Sn addition to β Ti-V alloys retards athermal ω transformation.[9,10] Referring to the references, the effect of Sn addition to β Ti-V alloys on Young's modulus was investigated. Figure 3 shows Sn content dependence of Young's modulus in β (Ti-20 mass%V)-x mass%Sn, where the ratio of Ti to V in mass% is kept constant even though Sn

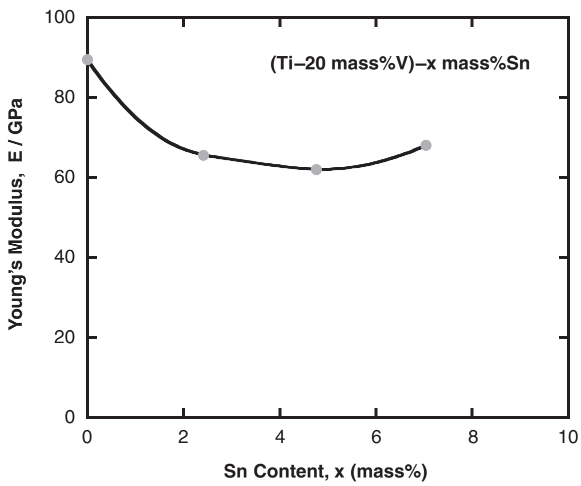

Fig. 3 Sn content dependence of Young's modulus in quenched Ti-V-Sn ternary alloys.

is added. Evidently, Young's modulus of β Ti-V alloys is decreased by alloying with Sn. A similar result was obtained in quenched β Ti-Nb-Sn alloys. When 2.5 mol%Sn was added to Ti-35 mass%Nb, martensitic transformation was confirmed to be completely suppressed by optical microscopy and athermal ω transformation was mostly suppressed as far as TEM observation was concerned. Young's modulus of (Ti-35 mass%Nb)-2.5 mol%Sn was 50.7 GPa, which was considerably lower than the minimum of a binary Ti-Nb alloy, 61.5 GPa. However, a further addition of 3.0 mol%Sn increased Young's modulus to 57.4 GPa in a similar way to Sn-added Ti-20 mass%V. Referring to the results shown in Figs. 1 and 2, the minimum in Young's modulus appears to be associated with the stability of β phase. Therefore, ternary alloy composition corresponding to low Young's modulus will be estimated by considering the stability of β phase.

The phase stability of Ti alloys has been calculated by Morinaga *et al.* based on the DV-Xα cluster method.[11)] In their calculation the two parameters, *Bo* and *Md*, are defined, where *Bo* is related to the strength of the covalent bonding between Ti and an alloying element and *Md* is correlated with the electronegativity and metallic radius of elements. According to the definition of the parameters, the average value of Bo for alloys should be as small as possible and the average value of *Md* for alloys should be as large as possible to attain low Young's modulus. Figure 4 shows changes in $\overline{Md}$-$\overline{Bo}$ relation of Ti by alloying. As can be seen in Fig. 4, V addition to Ti decreases $\overline{Md}$ without an appreciable change in $\overline{Bo}$. Young's modulus of Ti-V binary alloys containing from 20 to 42 mass%V is plotted as a function of $\overline{Md}$ in Fig. 5, where $\overline{Bo}$ is in the narrow range of 2.79 to 2.80. The minimum composition of Young's modulus corresponds to that in Fig. 1. At $\overline{Md}$ lower than the minimum where no athermal ω phase is formed on quenching, Young's modulus decreases with increasing $\overline{Md}$, consistent with the theoretical prediction.[2)]

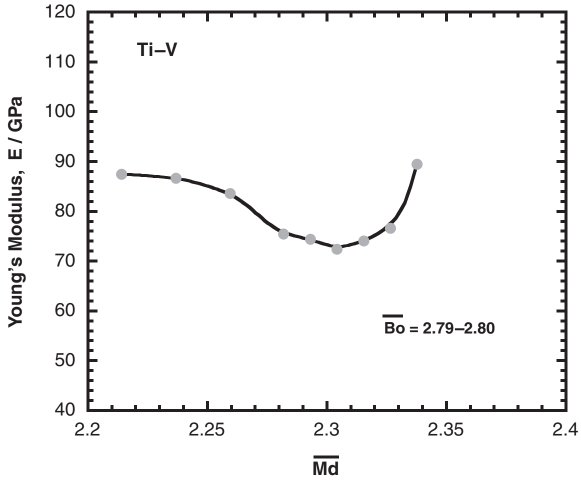

Fig. 5 $\overline{Md}$ dependence of Young's modulus in quenched Ti-V binary alloys.

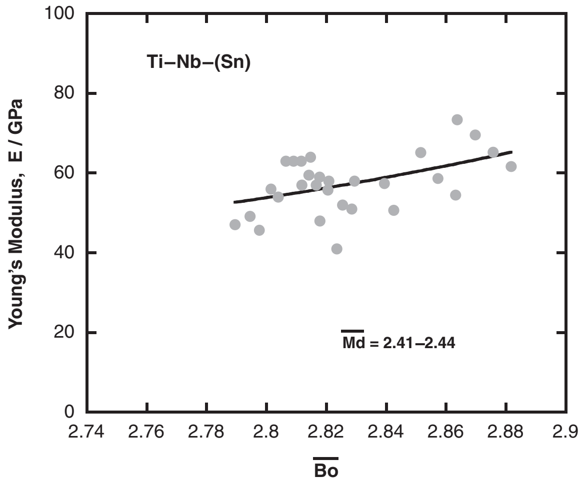

Fig. 6 $\overline{Bo}$ dependence of Young's modulus in quenched Ti-Nb-Sn ternary alloys.

Figure 6 shows $\overline{Bo}$ dependence of Young's modulus for Ti-Nb binary alloys and Ti-Nb-Sn ternary alloys which have $\overline{Md}$ values in the range of 2.41 to 2.44. Although considerable scattering is observed, one can see a tendency that Young's modulus decreases with decreasing $\overline{Bo}$, which is consistent with the theoretical prediction.[2)] The scattering would arise from differences in stability of β phase for the alloys used in this experiment. As shown in Fig. 2, the minimum in Young's modulus is sensitive to alloy composition in Ti-Nb alloys, as compared to Ti-V alloys. The distribution in the $\overline{Md}$ range of 2.41 to 2.44, which is employed in plotting the measured values in Fig. 6, would change the stability of β phase depending on alloy composition. Interestingly, Fig. 6 indicates that Young's modulus of β Ti-Nb-Sn alloys at room temperature can be decreased to about 40 GPa when alloy composition is optimized.

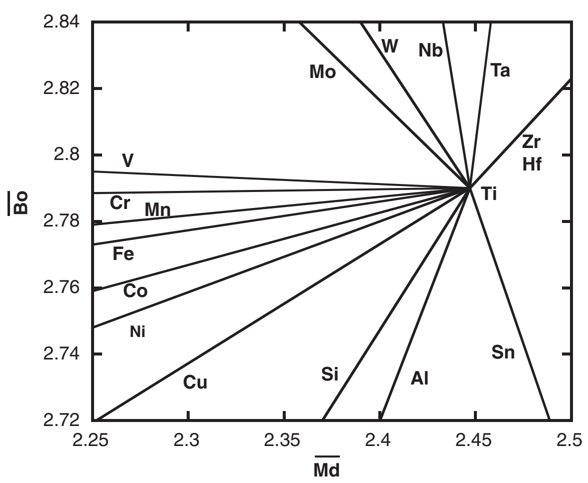

Fig. 4 $\overline{Bo}$-$\overline{Md}$ relations for various Ti binary alloys by Morinaga *et al.*[2)]

It should be noted that Young's modulus in Fig. 6 is summarized at room temperature as a function of alloy composition. All the quenched β alloys in Fig. 6 are unstable at room temperature, since neither martensitic transformation nor dominant athermal ω transformation is suppressed in the alloys by ice water quenching, and isothermal ω transformation occurs on aging at relatively low temperature. In addition, hcp α phase appears on prolonged aging at intermediate temperature or on slow cooling from high temperature. It has been reported that some Ti-Nb-Sn alloys with compositions similar to the present alloys undergo martensitic transformation by cooling below room temperature or applying a stress at room temperature, thereby inducing shape memory or superelasticity.[11] This means that the present alloys may undergo martensitic transformation by cooling below room temperature. It is generally accepted that elastic anisotropy exerts a significant effect on martensitic transformation and the anisotropy often increases with decreasing temperature towards martensitic transformation temperature. That is, the larger the elastic anisotropy of a parent phase becomes, the more easily the martensitic transformation takes place.[12] The present alloys exhibiting low Young's modulus, therefore, seem to possess considerable elastic anisotropy at room temperature. Unfortunately, there are no available data on the elastic anisotropy of β Ti-Nb and Ti-Nb-Sn alloys. For some Ti-Nb and Ti-Nb-Sn alloys we have measured Young's modulus in the 45° and 90° directions to the rolling direction as well as in the rolling direction and recrystallization texture to investigate the effect of elastic anisotropy on Young's modulus. It was found that β Ti-Nb-Sn alloys have considerably strong $\{110\}\langle 112\rangle$ texture, while β Ti-Nb binary alloys have very weak texture not clearly identified. This difference is not clearly understood at present, but ω phase included in the samples before cold rolling would be responsible for the different textures, since ω transformation is suppressed by the Sn addition. Another plausible explanation is that different solidification microstructures lead to the different textures, since the Sn addition significantly decreases melting temperature. In spite of the different textures Young's modulus of both the alloys is not so sensitive to the measured directions. Young's modulus is always the lowest in the rolling direction and an increase in Young's modulus in the 45° and 90° directions is about 10% or so. Thus, the composition dependence of Young's modulus compared in the rolling direction in this study is considered to demonstrate the intrinsic characteristics of β Ti-Nb and Ti-Nb-Sn alloys.

This work has finally focused on low Young's modulus in β Ti-Nb-Sn alloys. This is because the minimum value of Young's modulus in β Ti binary alloys is lower in Ti-Nb than in Ti-V. In addition, Ti, Nb and Sn are known to be non-cytotoxic. Therefore, β Ti-Nb-Sn alloys having low Young's modulus are expected to use as implants for human bones.

4. Conclusions

Young's modulus of β Ti-V-(Sn) and Ti-Nb-(Sn) alloys quenched after solution treatment was measured at room temperature as a function of alloy composition. The obtained results are summarized as follows.

(1) Composition dependence of Young's modulus in binary β Ti-V and Ti-Nb alloys exhibits a minimum arising from athermal ω phase formation at lower alloying contents and increase in β phase stability at higher alloying contents.

(2) Minimum composition in Young's modulus after aging moves toward higher alloying content, since isothermal ω transformation takes place depending on composition.

(3) Sn addition to binary Ti-V and Ti-Nb alloys decreases Young's modulus due to suppression or retardation of ω transformation.

(4) Low Young's modulus of about 40 GPa is obtained by controlling the composition in Ti-Nb-Sn.

(5) Composition dependence of experimentally measured Young's modulus accords qualitatively with the theoretical prediction.

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