Biomaterials Science: Processing, Properties and Applications III.
Edited by Susmita Bose, Amit Bandyopadhyay and Roger Narayan.

PHASE STABILITY AND YOUNG'S MODULUS OF Ti-Cr-Sn-Zr ALLOYS

Yonosuke Murayama*, Hiromasa Sakashita*, Daichi Abe*,
Hisamichi Kimura** and Akihiko Chiba**

*Niigata Institute of Technology, Kashiwazaki, Niigata, Japan
**IMR, Tohoku University, Sendai, Miyagi, Japan

ABSTRACT

In this study, The Young's modulus of Ti-Cr-Sn-Zr quaternary alloys exhibiting a wide compositional range was investigated. The quenched microstructure of these Ti-Cr-Sn-Zr quaternary alloys displayed a transition from martensitic structure to β phase structure depending on the amount of Cr and Zr. The Ti-Cr-Sn-Zr quaternary alloy with meta-stable β phase structure shows minimum values of both Young's modulus and tensile strength, although the Ti-Cr-Sn-Zr quaternary alloy with martensitic structure and stable β phase structure shows higher Young's modulus and strength. The Ti-Cr-Sn-Zr quaternary alloy with the meta-stable β phase shows two step yielding phenomenon in tensile stress-strain curves, in which first yield stress indicates the onset stress of a stress induced martensitic transformation and second yield stress indicates the onset of the slip deformation. The grain size of the Ti-2Cr-6Sn-45Zr quaternary alloy with meta-stable β phase structure influenced its mechanical properties. Although first yield stress decreased and the second yield stress increased when the grain size of this alloy diminished, Young's modulus and the super elastic properties were not influenced greatly.

INTRODUCTION

Metallic materials are used as the implant material more than ceramics and polymers, because they have reliable mechanical properties such as the strength and the toughness. Though metallic materials have excellent mechanical properties, they must satisfy the following three conditions as implant materials. 1. Alloys are formulated using noncytotoxic elements. 2. They have suitable surface structure and properties for contact with human body tissue. 3. Mechanical properties such as Young's modulus are desired to be close to the properties of human bone.

Metallic elements such as V, Co and Ni, which are currently used in implant materials, raise concerns of toxicity or allergic reactions if they elute as ions. Artificial implant material used in the human body should be designed using only noncytotoxic metallic elements, for example, Ti, Zr, Sn, Cr, Nb, Ta and so on[1].

High adhesive strength between an artificial implant material and human bone is desirable, if the implant material will be kept in the human body long term. A lot of study about the relation between surface properties and the cell multiplication is being conducted[2]. However, if the implant is short term in nature, then adhesive strength between implant material and the human bone should naturally be low. The ability of calcium phosphate formation between Ti and Zr is different[3], so that Zr may have lower adhesive strength than Ti, although both elements show excellent biocompatibility. This means that the Ti-Cr-Sn-Zr alloys with large different compositional ratio of Ti to Zr may show the large different properties as biomedical materials.

The Young's modulus of human bone is from 10GPa to 30GPa that is much lower than the metallic materials. The Young's modulus of SUS316 and Ti-6Al-4V alloy are, for example, 193GPa and 114GPa, respectively. The large difference of Young's modulus between the human bone and the implant material may cause stress shielding phenomenon, so that the new bone growth will be disturbed and the bone resorption will occur. Therefore, it is desirable to lower the Young's modulus of the metallic implant materials[4].

The apparent Young's modulus of a porous material is much lower than the solid bulk material[5]. However, the fatigue strength of porous materials is problematic, though porous structure near a bone surface has proven useful for both contact strength and remodeling. By the way, the Young's modulus of β stabilized Ti alloys quenched from the β field is much lower depending on the amount of β stabilizing element such as Nb, V or Cr[6]. Active research for meta-stable β Ti alloys based on Ti-Nb system alloys has been conducted for biomedical materials, because Nb is non-cytotoxic and meta-stable β Ti-Nb system alloys have a low Young's modulus[1, 4, 7-9]. However, Nb is a rare metal, expensive and also meta-stable β Ti-Nb alloys with low Young's modulus contain over 35Nb in mass%. The meta-stable β Ti-Nb alloy shows excellent workability but low tensile strength.

Cr is a β-eutectoid element, which stabilizes β phase of Ti. Cr has been proved to decrease the Young's modulus of meta-stable β Ti-Cr alloys, in a manner similar to Nb of β-isomorphous element in a Ti-Nb alloy[10, 11]. The amount of Cr required for low Young's modulus in Ti-Cr system alloys is much smaller than Nb in Ti-Nb system alloys, because Cr is more effective as β stabilizer. Ti-Cr-Sn alloy and Ti-Cr-Sn-Zr alloy show much lower Young's modulus in the narrow composition range for Cr but wide for Zr[12-14]. The Young's modulus of ternary and quaternary Ti-Cr based alloys is much lower than Ti-Cr binary alloys, because Sn and Zr suppress the athermal ω phase produced during quenching.

In this study, The Young's modulus of Ti-Cr-Sn-Zr quaternary alloys with a wide compositional range was investigated. The Ti-Cr based alloy with meta-stable β phase structure shows minimum values of both Young's modulus and tensile strength, although the Ti-Cr based alloy with martensitic structure and stable β phase structure shows higher levels. The grain size of Ti-Cr-Sn-Zr quaternary alloy with low Young's modulus was controlled by the deformation processing in this experiment. The effect of grain size on the mechanical properties of the Ti-Cr-Sn-Zr quaternary alloy with meta-stable β phase structure was investigated.

EXPERIMENTAL PROCEDURE

Ti-2~8mass%Cr-6mass%Sn-0~60mass%Zr alloys were prepared. The composition of all alloys in this experiment is indicated by mass%. The alloys with required compositions were prepared by the arc melting. Button ingots were melted in a copper hearth under an argon atmosphere. The arc-melted and sliced buttons with a thickness of about 8mm were hot rolled at 1073K in to a plate about 1.6mm thick. The tensile specimens were prepared from the arc-melted and rolled plates. They were sealed in a quartz tube under a vacuum of 2×10^{-3} Pa and were homogenized for 7.2ks at 1223K to obtain a β solid solution which was quenched into ice water by breaking the quartz tube immediately after quenching. The specimen of this processing is notated as HR 950.

The other rolling and heat treatment processing was conducted for Ti-2Cr-6Sn-45Zr alloy to make the grain size smaller. After arc melting, the sliced ingot was heat-treated homogeneously at 1223K for 72ks. The heat-treated ingot of Ti-2Cr-6Sn-45Zr alloy was cold rolled with intermediate heat treatment at 1073K. Then, the ingot was treated in a solid solution heat treatment at 1023K and 1073K for 1.8ks. The specimen obtained from this processing with intermediate heat treatment is notated as CR Int 750 and CR Int 800 due to the heat treatment temperature.

The microstructures of the specimen were identified by optical microscope. The constituent phases before and after deformation were evaluated by the X-ray diffraction analysis, in which a solid solution heat-treated plate specimen of 10mm square was used and 15% cold rolled. The mechanical properties were evaluated by a tensile test. The dimension of the tensile specimen is 2.5mm width and 1.5mm thickness. The gage length is 10mm. The mechanical test was conducted using the autograph of Shimadzu Co. (AG-IS10kN). The crosshead speed was constant, which became an initial strain rate of 1 x $10^{-4}s^{-1}$ when the plastic deformation behavior was evaluated. The Young's modulus was evaluated by a strain gauge pasted on the tensile test piece. Load was increased gradually and strain under the constant applied load was measured and the Young's modulus was calculated. Super-elasticity was evaluated by cyclic loading-unloading deformation of the tensile test piece with a strain gauge. All mechanical properties were measured at room temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the Young's modulus of Ti-Cr-6Sn-Zr alloys, changing the amount of Cr and Zr. The alloys, which Young's modulus is plotted by a solid mark in Fig. 1, were hot rolled and treated in a solid solution heat treatment at 1223K for 7.2ks (HR 950). The amount of Zr in the alloys that shows minimum Young's modulus is different depending on the amount of Cr. In the series of Ti-8Cr-6Sn-xZr (x=0~40mass%) alloys, the Young's modulus of Ti-8Cr-6Sn ternary alloy shows the minimum Young's modulus. Ti-8Cr-6Sn-xZr alloys consist of β phase regardless of the amount of Zr, since the amount of Cr is sufficient to stabilize β phase. In the series of Ti-5Cr-6Sn-xZr (x=0~40mass%) alloys, the Young's modulus of the alloys containing Zr of 10mass% and under is lower than the alloys with high amount of Zr. The quenched microstructure of the Ti-5Cr-6Sn ternary alloy is martensitic structure, though the microstructure of the Ti-5Cr-6Sn-Zr quaternary alloys containing Zr over 5mass% is β phase. Ti-5Cr-6Sn-5Zr alloy has a border composition where the quenched microstructure shift from martensite to β phase, and then the Young's modulus of Ti-5Cr-6Sn-5Zr alloy shows large dispersion. The Young's modulus of the alloy with the composition near the border shows low values. The

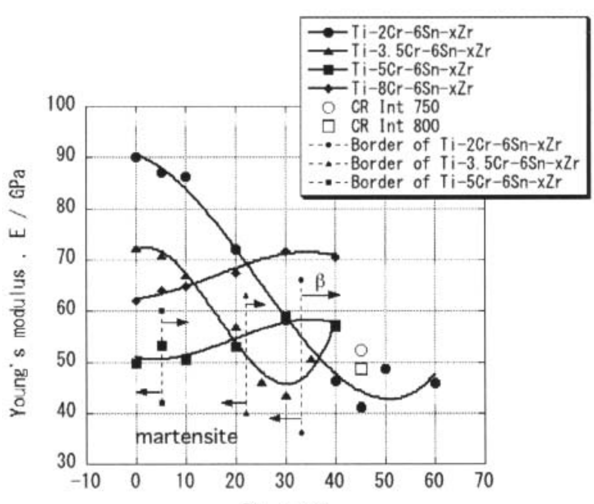

Figure 1. Compositional dependence of Young's modulus and as-quenched microstructure of Ti-Cr-Sn-Zr quaternary alloys.

amount of Zr in the alloy that shows minimum Young's modulus becomes larger with decreasing the amount of Cr. Simultaneously, the amount of Zr of the border composition where the quenched structure shift from martensite to β phase becomes larger.

In the series of Ti-2Cr-6Sn-xZr (x=0~60mass%) alloys, the amount of Zr in the border composition is between 30 and 40mass%, that is, as-quenched Ti-2Cr-6Sn-30Zr alloy shows martensitic structure. The alloy shows high deformation hardening in the tensile stress–strain curve because of the variant selection in martensite during tensile deformation. Ti-2Cr-6Sn-60Zr alloy deforms by slip deformation of β phase in tensile test, so that the alloy shows the high yield stress and less deformation hardening in the stress-strain curve. Ti-2Cr-6Sn-45Zr alloy shows two step yielding phenomenon in tensile stress-strain curve. The composition of T-2Cr-6Sn-45Zr alloy is a near border composition where the quenched microstructure shifts from martensite to β phase, so that the stress induced martensitic transformation becomes predominantly deformation mode because of the instability of β phase. Since first and second yield stresses indicate the onset stress of the stress induced martensitic transformation and the slip deformation respectively, the whole flow stress is lower than other alloys with martensitic or stable β phase structure in as-quenched condition.

Fig. 1 shows also the Young's modulus of CR Int 750 and CR Int 800 of the Ti-2Cr-6Sn-45Zr alloy, and their comparison to the Young's modulus of HR 950 of the Ti-2Cr-6Sn-45Zr alloy. The Young's modulus of the alloy prepared by cold rolling with intermediate heat treatment, CR Int 750 and CR Int 800, is a little higher than the hot rolled without intermediate heat treatment, HR 950.

The grain size of the alloy that was hot rolled at 1073K and treated in the solid solution treatment at 1223K is about 600μm. Fig. 2 shows the optical microstructures of as-quenched CR Int 750 and HR 950 of Ti-2Cr-6Sn-45Zr alloys. The optical microstructure of CR Int 800 is almost same with CR Int 750. The grain size of CR Int 750 and CR Int 800 is about 110 μm and 150 μm respectively, which is much smaller than HR 950 of Ti-2Cr-6Sn-45Zralloy. Though the small black particles are observed in the optical microstructure, they are confirmed as etching pits in high magnification. No precipitation can be seen at the scale of the optical microscope, though some athermal ω phase may exist. The optical microstructure of HR 950 of Ti-2Cr-6Sn-45Zr alloy shows uniform contrast but CR Int 750 of Ti-2Cr-6Sn-45Zr alloy shows both dark and bright grains in the micrograph.

Fig. 3 shows the engineering stress – engineering strain curves of HR 950 and CR Int 750 of Ti-2Cr-6Sn-45Zr alloy. Both stress–strain curves of HR 950 and CR Int 750 show two step yielding phenomenon, that is, Ti-2Cr-6Sn-45Zr alloy deforms by stress induced martensitic transformation regardless of the grain size. Fig. 4 shows the optical micrographs of the HR 950 and CR Int 750 after tensile test until failure. The twin like deformation structure due to the

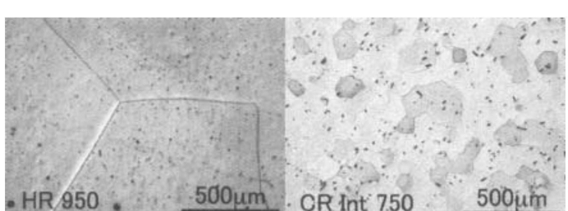

Figure 2. Optical micrographs of as-quenched HR 950 and CR Int 750 of Ti-2Cr-6Sn-45Zr alloys.

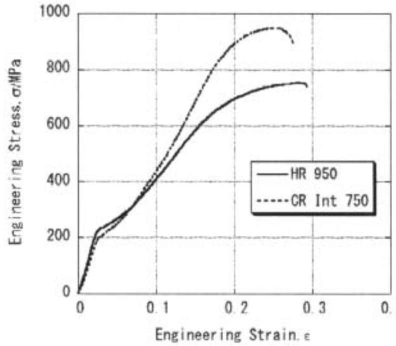

Figure 3. Enineering stress – Engineering strain curves of HR 950 and CR Int 750 of Ti-2Cr-6Sn-45Zr alloys.

stress induced martensitic transformation can be seen. The different variant orientation from the interior part of the grain appears to be acting along the grain boundary. The stress induced martensitic transformation may occur along grain boundaries due to the stress concentration.

First yielding stress that is the onset stress of the stress induced martensitic transformation in Fig.3 is different between the HR 950 and CR Int 750. The larger the grain size of the alloy is, larger the onset stress for the stress induced martensitic transformation is needed. If the stress induced martensitic transformation occurs at grain boundaries, transformed martensitic structure may spread toward interior grain from the grain boundary. The time when the whole grain is covered by transformed martensitic structure and the specimen shows the yielding might be more rapid in an alloy with small grain size than one with large grain size.

On the other hand, the relation between grain size and the second yielding stress is completely contrary to the relation between the grain size and the first yielding stress, that is, the larger the grain size of the alloy is, the smaller the second stress is. The relation between grain size and the second yielding stress reflects the Hall-Petch relation, because the second yielding stress indicates the onset stress of the slip deformation. The ultimate tensile stress of the CR Int 750 of Ti-2Cr-6Sn-45Zr alloy far exceeds 900MPa that is higher than Ti-6Al-4V alloy conventionally used as biomedical material.

Fig. 5 shows the X-ray diffraction profiles of the HR 950 of Ti-2Cr-6Sn-45Zr alloy before and after rolling deformation. As-quenched HR 950 consists only of meta-stable β phase and may have strong texture, because only β (110) peak can be seen. The X-ray diffraction

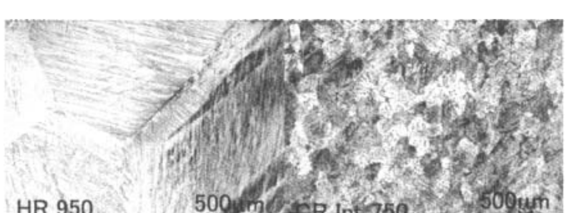

Figure 4. Optical micrographs of HR 950 and CR Int 750 of Ti-2Cr-6Sn-45Zr alloys after tensile test until failure.

profile of as-quenched CR Int 750 of Ti-2Cr-6Sn-45Zr shows two peaks of β (110) and β (112), as shown in Fig. 5. The Young's modulus of CR Int 750 and CR Int 800 of Ti-2Cr-6Sn-45Zr alloy was a little higher than HR 950 of Ti-2Cr-6Sn-45Zr alloy, as shown in Fig. 1. It may be one reason that the texture of the alloy processed through intermediate heat treatment is weaker than the alloy processed without intermediate heat treatment. However, the difference of the Young's modulus between HR 950 and CR Int 750 is small in scattering range, because the values are close to the Young's modulus of HR 950 of Ti-2Cr-6Sn-50Zr alloy in Fig. 1.

After cold rolling of the solid solution heat-treated alloy, many peaks were appeared as shown in Fig. 5. The positions of peaks are the same in HR 950 and CR Int 750. The many peaks after cold rolling resulted from the stress induced martensitic transformation. When the element of β stabilizer is alloyed in Ti and quenched from β phase field, the quenched microstructure changes depending on the amount of β stabilizer. The hexagonal α' martensite is formed in the binary alloy with low content of β stabilizer. With increasing the amount of β stabilizer, the orthorhombic α" martensite and the β appears in the order, though the athermal ω was formed competitively. The martensitic transformation related to the shape memory properties, super-elastic properties and low Young's modulus is regarded as orthorhombic α" matensitic transformation, because α" competes with meta-stable β in similar composition.

Fig. 5 indicates the positions of peaks of α', α" and β phases, respectively. Since super-elastic properties was observed in HR 950 and CR Int 750 as shown in Fig. 6, the stress-induced martensite in this experiment may be the orthorhombic α" martensite. However, the number of peaks are small and peak positions may coincide with the indices of hexagonal α' martensite. Hanada et al. studied extremely the effect of the alloying elements on the deformation mode and β phase stability of meta-stable β Ti alloys[15]. They indicated that the element of Sn and Al restrains the athermal ω transformation and promotes the orthorhombic α" martensitic transformation in the meta-stable β Ti alloys. Thus, the orthorhombic α" martensitic transformation occurred in Ti-7Cr-4Sn and Ti-7Cr-4Zr ternary alloys. However, They showed that the hexagonal α' martensitic transformation occurred in the Ti-7Cr-1.5Al-4Zr quaternary alloy. The crystallographic competitive relation of stress induced α' and α" martensite in meta-stable β phase of ternary and quaternary Ti alloys is unclear at present.

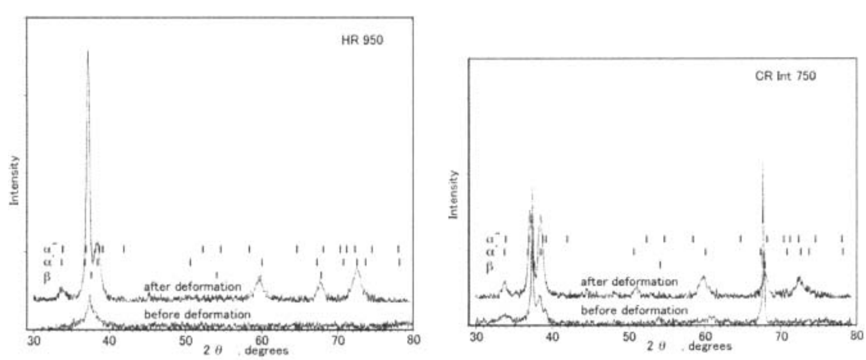

Figure 5. X-ray diffraction profiles of the HR 950 and CR Int 750 of Ti-2Cr-6Sn-45Zr alloy before and after rolling deformation.

Fig. 6 shows the stress–strain curves of HR 950 and CR Int 750 of Ti-2Cr-6Sn-45Zr alloy in the cyclic loading and unloading deformation. The remarkable super-elasticity was observed in both alloys, in which recovery of elastic strain is about 3%. The recovery of elastic strain is larger than Ti-6Cr-3Sn ternary alloy[16]. The onset stress of stress induced martensitic transformation in first cycle is larger in alloy of HR 950 than CR Int 750, which relation is same as shown in Fig. 3. However, the deformation behavior after second cycle is different between HR 950 than CR Int 750, that is, the flow stress of HR 950 shows steps at the intersection with former cycle, though the flow stress of the CR Int 750 ties continuously in cycles. The apparent Young's modulus of HR 950 and CR Int 750 is estimated to be approximately 15GPa that is similar to human bone, taking account of the recovery of elastic strain by super-elasticity.

CONCLUSION

The Young's modulus of Ti-Cr-Sn-Zr quaternary alloys depends on the amount of Cr and Zr. The Ti-Cr-Sn-Zr quaternary alloys with meta-stable β phase, which composition is close to the structural transition from martensite to β phase, show much low Young's modulus and stress induced martensitic transformation. The Ti-Cr-Sn-Zr quaternary alloys with meta-stable β phase were obtained in large different compositional ratio of Ti to Zr.

The grain size of the Ti-2Cr-6Sn-45Zr quaternary alloy with meta-stable β phase structure influenced the mechanical properties. The onset stress of the stress induced martensitic transformation decreases and the onset stress of the slip deformation increases, when the grain size of the alloy became small. The Young's modulus and the super elastic properties were not influenced so much.

REFERENCES

1 D.Kuroda, M.Niinomi, M.Morinaga, Y.Kato and T.Yashiro, Design and mechanical properties of new b type titanium alloys for implant materials, *Mater. Sci. Eng.*, A243, 244-249 (1998)

2 S.Nishiguchi, S.Fujibayashi, H.M.Kim, T.Kokubo and T.Nakayama, Biology of alkali- and heat treated titanium implant, *J.Biomed Mater Res*, A67, 26-35 (2003)

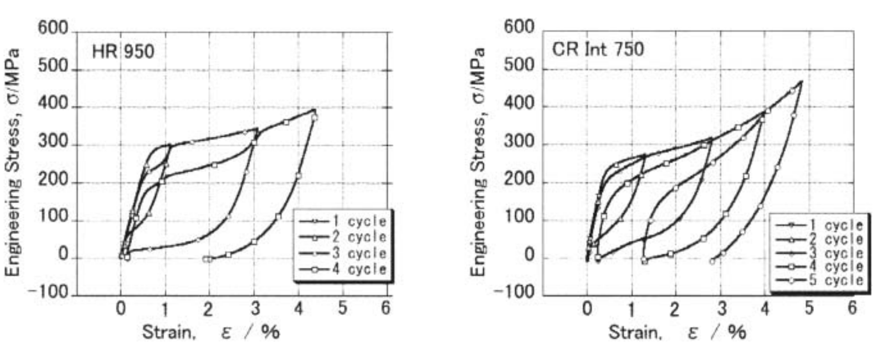

Figure 6. Stress-strain curves of HR 950 and CR Int 750 of Ti-2Cr-6Sn-45Zr alloy in the cyclic loading and unloading deformation.

[3] Y.Tsutsumi, D.Nishimura, H.Doi, N.Nomura and T.Hanawa, Differece in surface reactions between titanium and zirconium in Hanks' solution to elucidate mechanism of calcium phosphate formation on titanium using XPS and cathodic polarization, *Mater. Sci. and Eng. C*, 29, 1702-1708 (2009)

[4] T.Ahmed, M.Long, J.Silvestri, C.Ruiz and H.J.Rack, A new low modulus, biocompatible titanium alloy, *Titanium '95:Science and Tecnology*, the 8th World Conference on Titanium held at Birmingham, UK, 1760-1767 (1995)

[5] I.H.Oh, N.Nomura and S.Hanada, Microstructures and mechanical properties of porous titanium compacts prepared by powder sintering, *Mater. Trans.*, 43, 443-446 (2002)

[6] S.G.Fedotov, Mechanical and technological properties of titanium alloys, *Titanium and its Alloys*, I.I.Kormilkov, Ed., Akademiya Nauk SSSR, (transl. IPST. Cat. No.1415, 1966), 199-215 (1963)

[7] T.Ozaki, H.Matsumoto, S.Watanabe and S.Hanada, Beta Ti alloys with low Young's modulus, *Materials Trans.*, 45, 2776-2779 (2004)

[8] X.Tang, T.Ahmed and H.J.Rack, Phase transformation in Ti-Nb-Ta and Ti-Ta-Nb-Zr alloys, *J.Mat.Sci.*, 35, 1805-1811(2000)

[9] H.Matsumoto, S.Watanabe and S.Hanada, Beta TiNbSn alloys with low Young's modulus and high strength, *Mat.Trans.*, 46, 1070-1078 (2005)

[10] Y.Murayama, S.Sasaki, S.Rajanapolan, D.Huber, H.Kimura, A.Chiba and H.L.Fraser, Mechanical properties and phase stability of Ti-Cr system alloys, *Proceedings of TMS 138th Annual Meeting & Exhibition*, vol.3, General Paper Selections, 263-270 (2009)

[11] Y.Murayama, S.Sasaki, H.Kimura and A.Chiba, Mechanical properties of Ti-Cr-Sn-Zr alloys, *Materials Science Forum*, vol. 638-642, 635-640 (2010)

[12] Y.Murayama, S.Sasaki, H.Kimura and A.Chiba, Phase stability and mechanical properties of Ti-Cr based alloys with low Young's modulus, *Materials Science Forum*, vol. 654-656, 2114-2117 (2010)

[13] Y.Murayama, H.Kimura and A.Chiba, Young's modulus of Ti-Cr-Sn-Zr alloys with meta-stable beta phase, *Proceedings of the 12th World Conference on Titanium*, edited by L.Zhou, H.Chang, Y.Lu and D.Xu, The Nonferrous Metals Society of China, vol. III., 2180-2183 (2012)

[14] Y.Murayama, H.Sakashita, H.Kimura and A.Chiba, Mechanical properties of Ti-Cr-Sn-Zr alloys with low Young's modulus, *Materials Science Forum*, vol. 706-709, 553-556 (2012)

[15] S.Ishizaki, S.Hanada and O.Izumi, Effect of Zr, Sn and Al additions on deformation mode and beta phase stability of metastable beta Ti alloys, *ISIJ International*, 31, 807-813 (1991)

[16] A.Wadood, T.Inamura, H.Hosoda and S.Miyazaki, Ageing behavior of Ti-6Cr-3Sn β titanium alloy, *Mater. Sci. Eng A*, 530, 504-510 (2011)