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Influence of aging heat treatment on mechanical properties of biomedical Ti–Zr based ternary alloys containing niobium

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Titanium–zirconium based alloys containing a small amount of niobium were investigated in order to evaluate their possible use as biomedical materials. Zirconium, which belongs to the IVa group, is known to have good corrosion resistance and biocompatibility similar to titanium. As the titanium–zirconium system shows a complete solid solution, a wide variation of alloy design is available and large quantities of solid-solution hardening must be possible. Niobium, having a β-phase stabilizing effect, was chosen as a ternary element in order to control desirably the microstructure. There have been no reports which suggest its harm to a living body. The alloys containing 2% or 3% niobium showed the highest hardness value after aging heat treatment at 773 K. In contrast to this, no alteration of hardness was seen in specimens aged at 1073 K. Through conventional X-ray diffractometry and *in situ* X-ray analysis using a hot stage, β-phase precipitation in the α matrix was identified. From the above results, it is concluded that alloys containing 2%–3% niobium are hopeful candidates for new kinds of biomedical alloys, when they are heat treated under suitable conditions. © *1998 Kluwer Academic Publishers*

1. Introduction

Titanium and its alloys are still attracting much attention for application as biomedical metallic materials. Their properties, such as relatively low density, high corrosion resistance and satisfactory biocompatibility, are desirable in this respect. Many biomedical applications which use titanium alloys, and in particular Ti–6Al–4V, are found in orthopaedic surgery, where relatively low modulus and equivalent strength properties in comparison to stainless steels or cobalt chromium alloys are considered advantageous. However, titanium produces adverse tissue reaction from fretting of the metal and it shows relatively poor wear resistance in an articulating situation. The addition of aluminum and vanadium as alloying elements have been considered in order to provide a desirable $\alpha + \beta$ two-phase structure due to their α and β stabilizing effects, respectively. Additionally, alloying with aluminum gives a high rate of solid-solution hardening to the titanium matrix. In the engineering field, especially aero-space engineering, the alloying of these two elements is necessary to obtain titanium alloys with sufficiently high mechanical properties.

Ti–6Al–4V has been introduced as a biomedical material in place of more established alloys, such as stainless steels or cobalt chromium alloys. Although the alloy has sufficient strength for orthopaedic devices, the addition of the toxic elements has not yet been fully evaluated. The use of both aluminum and vanadium as alloying elements is now seen as undesirable, hence there is an opportunity to develop alternative titanium alloys, with neither aluminum nor vanadium. To extend the application of titanium alloys as biomedical materials, it is necessary to develop new alloys which are sufficiently strong, stable in a corrosive environment, have satisfactory biocompatibility, and safe for use *in vivo*.

Some studies have been conducted to develop new biomedical titanium alloys with neither aluminum nor vanadium. A Ti–6Al–7Nb alloy, having an $\alpha + \beta$ two-phase structure, the same as Ti–6Al–4V alloy, is one solution [1]. This alloy has formulated to replace vanadium in Ti–6Al–4V alloy with niobium to act as a β stabilizer in titanium alloys, thereby providing improved mechanical properties. Sufficient niobium was alloyed to create mechanical properties sufficient for artificial hip joints, as classified by ASTM in wrought implant material [2]. Niobium is considered less harmful compared to vanadium in the previous studies [3]. Some efforts to develop new alloy designs other than this have also been reported. Recently, Ti–15%Zr–4%Nb–2%Ta–0.2%Pd alloy [4] and

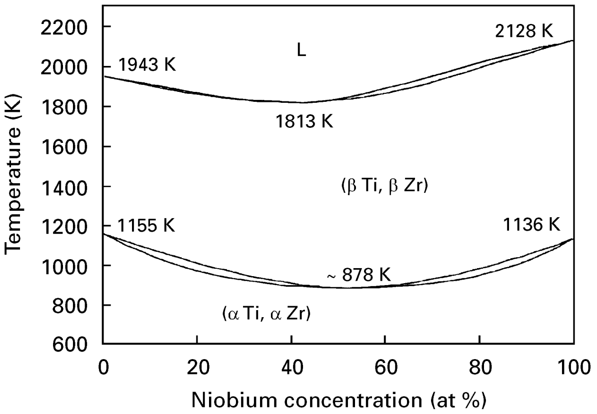

Figure 1 The Ti–Zr binary phase diagram, after Murray [6]. This system shows the complete solid solutions in both higher β (b c c) phase and lower α (h c p) phase.

Ti–5%Al–3%Mo–4%Zr alloy [5] (in weight per cent) have been developed. In both studies, vanadium was eliminated due to its cytotoxicity, and niobium and molybdenum were added as the β stabilizer. Zirconium is used in its role for solid-solution hardening.

Zirconium, which belongs to the IVa group together with titanium, is known to show chemical properties similar to titanium. Its physical properties are also similar to those of titanium, for example the allotropic transformation in solid phases occurs between higher b c c and lower h c p phases. As indicated in Fig. 1 [6], because the titanium–zirconium binary system shows a complete solid solution, a wide variation of alloy design is available, and large quantities of solid-solution hardening might be expected. The authors have previously reported that the highest hardness and strength are obtained for the alloy with composition 50%Ti–50%Zr (compositions of the alloys will be referred to atomic per cent hereafter) in this binary system, and have revealed its superior potential as the base material for alloy design as a new biomedical material [7, 8]. It has been confirmed that the Ti–Zr binary alloys showed superior corrosion resistance and biocompatibility in a recent study [9].

In this study, titanium–zirconium based alloys containing small amounts of niobium were investigated in order to evaluate their possible application as a biomedical material. Niobium, having a β-phase stabilizing effect for both titanium and zirconium, was chosen as a ternary element to control microstructure desirably. Microstructure control was carried out by aging heat treatment at various temperatures. Phase relations of the alloys were examined using X-ray diffractometer techniques. Finally, the relationships between heat treatment and mechanical properties were revealed and are discussed in detail.

2. Experimental procedure

Alloys with an equi-atomic composition of titanium and zirconium were used. Amounts between 0 and 5 at % niobium were added as a ternary alloying element. Alloys containing 20%–50% niobium were also used to measure the lattice parameters in order to confirm the distribution behavior of the ternary element in the two-phase structure. All the alloys were prepared from sponge titanium (> 99.8 wt% purity), sponge zirconium (> 99.5 wt %) and niobium (> 99.5 wt %) by arc melting with a non-consumable tungsten electrode under a highly inert atmosphere of high-purity argon gas which was deoxidized by heating over getter titanium prior to melting. Arc discharges were applied to the raw materials placed on a water-chilled copper hearth. The ingots were turned over and remelted at least five times in order to obtain ingots homogeneous in composition and microstructure. The button ingots were approximately 20 g in weight.

The ingots were homogenized at 1273 K for 24 h in vacuum, at a pressure less than 5×10^{-3} Pa, followed by furnace cooling. Aging heat treatment at 773 and 1073 K for several hours to control microstructures was subsequently conducted. The temperatures of heat treatment, 773 and 1073 K, were carefully chosen to provide α + β two-phase structure and β single-phase structure, respectively, according to the ternary phase diagrams proposed by Collings [10], which are shown in Fig. 2. The conditions of the heat treatment are shown schematically in Fig. 3. The average cooling rate of furnace cooling from 1073 K to 773 K was approximately $1.0\ \mathrm{K\,s^{-1}}$. Microstructures of the alloys observed using scanning and transmission electron microscopes have been discussed in a previous paper [11].

X-ray diffraction analysis was carried out to identify phase constitution (D5000, Siemens) and to measure lattice parameters (PW1700, Philips) of the as-homogenized and as-aged alloys at room temperature using CuK_α radiation. Additionally, hot-stage X-ray diffraction was conducted in a nitrogen-flow atmosphere using a sample which showed the α single phase at room temperature in order to confirm *in situ* phase alteration during aging heat treatment at 773 K. The 2 θ range, 52°–57°, was selected to identify the β-phase precipitation in the α matrix. The high-temperature X-ray diffraction measurement was carried out once an hour for up to 17 h. Each measurement took approximately 10 min. For this measurement, a very thin (0.1 mm) and small specimen was used to ensure the heat conductivity from the heater on the stage.

Hardness measurements were conducted to estimate the effect of aging heat treatment on the alloys' mechanical properties using a micro-hardness tester with a trigonal diamond indentor (DUH-200, Shimadzu). The hardness value from this tester, indicated as DH, is defined as a ratio of load and surface area of an impression marked by an indentor on the specimen's surface, using the same principle as the conventional Vickers hardness [12]. The diamond pyramid indentation is controlled electro-magnetically at a fixed loading rate, in this case, at $1.41 \times 10^{-2}\ \mathrm{N\,s^{-1}}$, to a designated load, 0.49 N, and kept at this load for a fixed time, 10 s. The surface area of impression after the indentation is calculated geometrically from the indentation depth and pyramid's dimensions. Because the indentation depth is

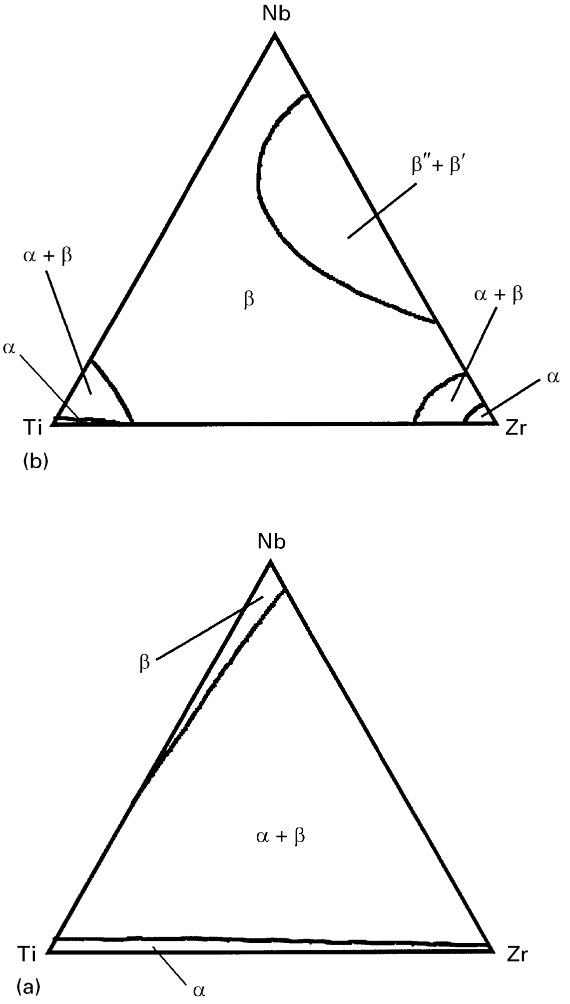

Figure 2 Isothermal cross-sections at (a) 773 and (b) 973 K of the Ti–Zr–Nb ternary phase diagram proposed by Collings [10]. Compositions investigated in this study are seen to be positioned in the α + β two-phase field and the β single phase field, respectively.

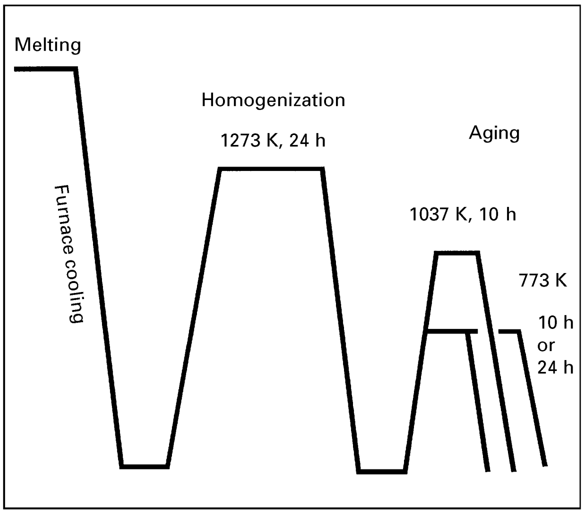

Figure 3 Schematic diagrams of homogenizing and aging heat treatment of the alloys. Each step of the heat treatment is followed by furnace cooling with an average cooling rate of approximately 1.0 K s^{-1}.

measured automatically by a differential transducer mounted on this tester, it eliminates personal errors during measurement. It was reported that the hardness obtained from this tester showed almost the same absolute value to those from a conventional Vickers hardness tester in previous work [7, 13].

3. Results

3.1. Hardness measurement of aged alloys

The highest hardness occurs at approximately 50%Ti–50%Zr in the Ti–Zr binary system [7]. The hardness recorded is around 250 DH while pure titanium and pure zirconium show values of about 100 DH. The same trends have been reported by other investigators for swaged or dental-cast Ti–Zr binary alloys [14–16].

The hardness of as-cast and as-aged ternary alloys aged at 773 K are shown in Fig. 4. For the as-cast alloys, the specimen containing 2% niobium shows the highest hardness, which has a hardness approximately 20% higher than binary alloy. After 10 h aging heat treatment at 773 K, the hardness of each alloy increased by 25%–55% (average 35%) as compared to the as-cast specimen. The highest hardness for all heat treatments is seen at the composition around 1%–2% niobium. By prolonged aging heat treatment up to 24 h, the hardness dropped again but was still approximately 20% higher than for the as-cast specimen, on average. In contrast, aging at 1073 K showed no considerable increase in hardness with niobium content, as shown in Fig. 5.

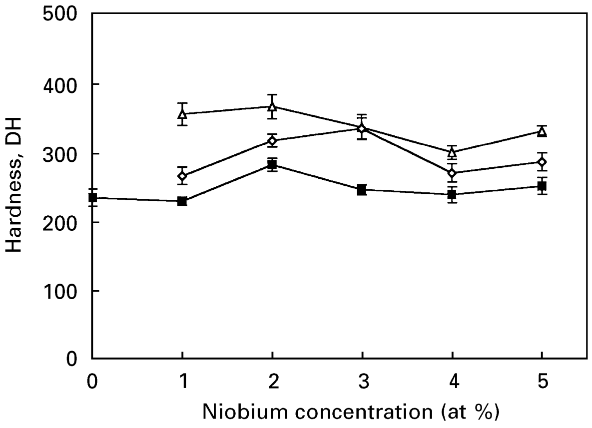

Figure 4 Hardness of the alloys containing niobium aged at 773 K compared with that of the as-cast alloys. Increasing hardness is seen in all the alloys tested (■) As-cast; (△) 773 K, 10 h; (◇) 773 K, 24 h.

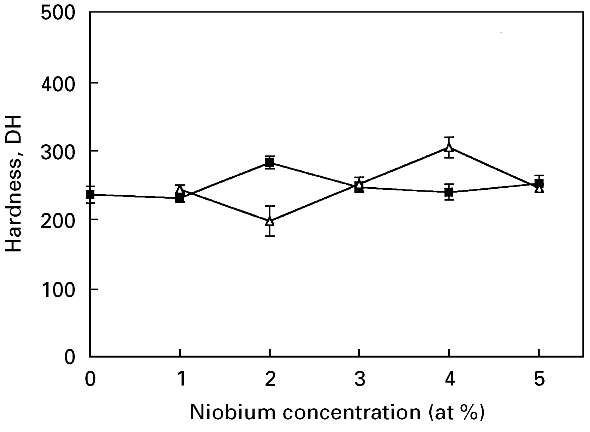

Figure 5 Hardness of the alloys containing niobium aged at 1073 K. No significant change is seen. (■) As-cast, (△) 1073 K, 10 h.

3.2. X-ray diffraction

Overall X-ray diffraction patterns of the specimens containing 2% Nb are exhibited in Fig. 6. The result of the alloy after homogenization heat treatment followed by furnace cooling is shown in (a), and after aging heat treatment at 773 K for 10 h, in (b).

While peaks from the specimen without the aging heat treatment can be analyzed as a series of typical α single phase peaks (a), the profile of the specimen aged at 773 K shows that it obviously contains additional peaks corresponding to the β-phase along with those from α. The different relative intensities observed in Fig. 6a and b, especially in the 2θ range 30–40°, is due to preferred orientation within the samples.

3.3. Lattice parameter measurement

Fig. 7 indicates the lattice parameters of β-phase measured in the present study together with that of pure niobium [17, 18] and Ti–50%Zr [19] (β-phase) taken from references to explain the so-called Vegard's law line in this pseudo-binary system. Note that data on 0% Nb, which is taken from the reference of Duwez [19], indicates the lattice constant of Ti–50%Zr binary alloy, because all the alloys contain the same amount of titanium and zirconium atoms and the abscissa indicates the niobium concentration added. For example, the alloy indicated as 40% Nb has the actual composition of 30%Ti–30%Zr–40%Nb.

In order to obtain β-phase as a part of α + β two-phase structure in the binary alloy, quenching from 1253 K had been carried out. The alloy containing 2%Nb was examined after aging heat treatment at 773 K to provide α + β two-phase structure. Other alloys having 20%–50%Nb were tested after homogenization. In the present work, the lattice constants of the ternary alloys showed generally good correspondence to Vegard's law, though a slight shift was seen in the alloys containing relatively lower niobium concentration.

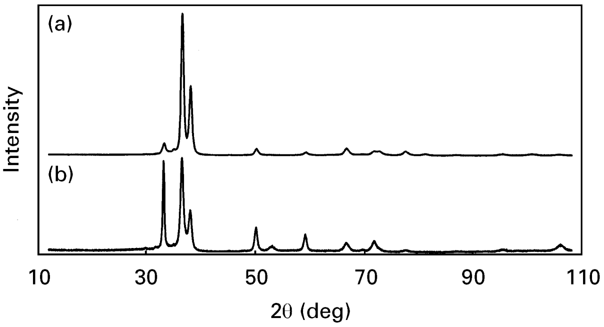

Figure 6 Results of the X-ray diffractometry carried out using the Ti–Zr–2% Nb specimens after (a) homogenization and (b) aging heat treatment at 773 K for 10 h, showing diffraction patterns from α single phase and α + β two-phase structures, respectively.

3.4. Hot-stage X-ray diffraction

It was confirmed that the X-ray diffraction pattern of 2%Nb specimen aged at 773 K for 10 h consisted of peaks from both α- and β-phases, while the homogenized specimen exhibits the α single phase, Fig. 6. In order to reconfirm the phase alteration during aging heat treatment at 773 K, hot stage *in situ* X-ray diffractometry was carried out using a high-temperature stage mounted on the X-ray diffractometer in a nitrogen flow atmosphere. The measurement was carried out at 773 K over a period of 17 h, and results are shown in Fig. 8 together with a diffraction pattern measured at room temperature. After the experiment, the sample looked slightly tarnished as if it had oxidized slightly, although there was no obvious evidence of oxidation in the diffraction data.

The peak corresponding to the β-phase (a small spiky peak at 54°) appeared clearly in the pattern taken after 5 h aging and the strength of the diffraction peaks seems to be saturated shortly after 6–7 h. This illustrates that the β-phase precipitates in the α matrix during aging heat treatment at 773 K resulting in α + β two-phase structure. These results are

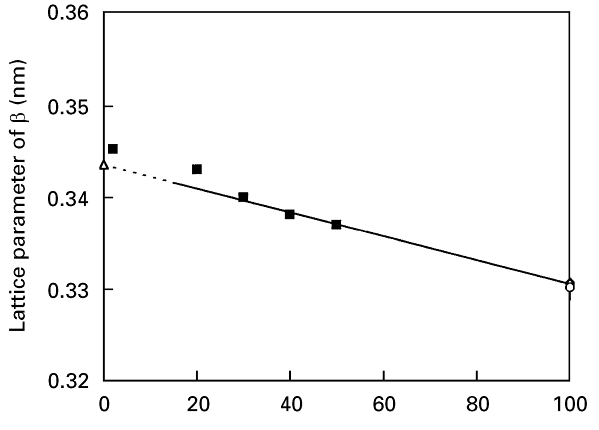

Figure 7 Lattice parameter alteration of the alloy in the Ti–Zr–Nb ternary system along with the pseudo-binary system from the niobium corner to the point of Ti–50% Zr on the Ti–Zr edge, showing Vegard's law line taken from (○) [17], (◇) [18] and (△) [19]. (■) Present work.

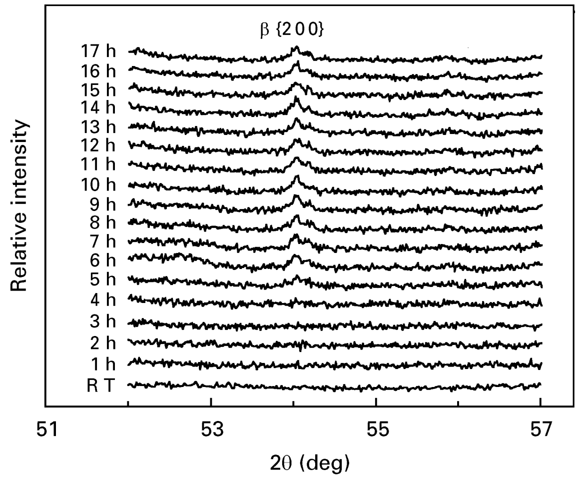

Figure 8 Diffraction patterns of the specimen containing 2% Nb showing phase alteration during aging at 773 K obtained using the hot-stage *in situ* X-ray diffractometer. The measurement was continued up to 17 h in a nitrogen flow atmosphere.

consistent with the results from conventional X-ray analysis of the alloys after aging heat treatment.

4. Discussion

In the present study, a Ti–Zr binary alloy having equiatomic per cent of both elements was chosen as a starting composition for ternary alloy design due to its advantage in hardness among all the alloys in this binary system. Fortunately, both titanium and zirconium have very similar chemical and physical properties, and most of these properties are desirable in a biomedical material. Furthermore, it was found that these features, such as superior corrosion resistance, excellent biocompatibility and phase relationships which are hoped will provide suitable microstructure, are retained over the whole binary system, which shows complete solid solution. In other words, there will be an opportunity to arrange the optimum mechanical properties by controlling the microstructure and to afford good chemical properties, the same as titanium itself, to the newly developed Ti–Zr based alloys.

4.1. Mechanical properties of aged specimens

As in the case of the design of Ti–6Al–4V, the conventional titanium alloy, some β stabilizing elements are required to control the phase constitution to the desirable $\alpha + \beta$ two-phase structure in the Ti–Zr based alloy. In this study, niobium was chosen as the β stabilizing ternary element. As a first step in this kind of alloy design, an optimized quantity of the alloying element has to be established, it is and more important, in the case of alloy design using only the β stabilizing element, without any α stabilizers. However, in the cases of Ti–6Al–4V and Ti–6Al–7Nb alloys, 6 wt % aluminum is balanced by 4 wt % vanadium or 7 wt % niobium to produce the two-phase structure. In the present study, because no α stabilizer was added, the ideal composition to produce the best microstructure is decided by only the amount of the β stabilizer, namely niobium.

As shown in Fig. 4, the alloys containing 1%–2% niobium exhibit the highest hardness in the range examined in this study, for both specimens without any heat treatment and with aging at 773 K. This niobium concentration, 1%–2%, is slightly less than for the Ti–6Al–7Nb alloy, which actually contains around 3.6 at % niobium together with 10 at % aluminum. It is appropriate to consider that lack of α stabilizer to counter the niobium may result in less niobium being required to make a desirable structure. Here, zirconium has no effect on the stabilization of any phase.

Considering the phase identification by X-ray diffractometry for the alloy with no heat treatment, indicated in Fig. 6a, the hardness of the as-cast alloys can be explained by the solid-solution hardening of niobium rather than the two-phase microstructure. The microstructural observations carried out previously using the as-cast alloys containing 1% and 2%Nb support this framing [11]. An increase in the hardness was achieved after the aging heat treatment at 773 K, because this aging heat treatment produces an $\alpha + \beta$ two-phase structure which is desirable to provide good mechanical properties. The X-ray results shown in Fig. 6b supported this.

As shown in Fig. 5, there is no significant change in the hardness of the alloys aged at 1073 K, where there is a β single-phase field according to Fig. 2. It can thereby be concluded that furnace cooling from the β-phase field may produce an α (strictly, Widmanstätten α, considering the cooling rate) phase structure regardless of the conditions before cooling, i.e. cooling down directly from melting or cooling after heat treatment.

4.2. Lattice parameter and phase occupation of ternary atoms

In a previous paper, we reported that niobium atoms had a tendency preferentially to occupy the β-phase in two-phase alloys shown in transmission electron micrographs and by EDX analysis [11]. To reconfirm this, lattice parameter measurement was carried out. As shown in Fig. 7, lattice constants measured in the present study generally show good correspondence with Vegard's law described by connecting data from pure niobium to Ti–50%Zr (β-phase) taken from the references. In the case of alloys with higher niobium concentration, a good agreement with Vegard's law is seen.

This consistency indicates that all of the added niobium atoms act to reduce the lattice constant of the β-phase, in other words, the niobium occupies the β-phase, because the lattice parameter alteration is parallel to the difference in atomic diameters.

For alloys with a relatively lower niobium concentration, 2% and 20%Nb, which have a two-phase structure, these show a slight shift toward larger parameter than predicted from Vegard's law. However, considering that the lattice constant of the Ti–50%Zr alloy in the reference was measured after quenching to provide a metastable phase, detailed discussion on this slight shift cannot be made here.

4.3. *In situ* measurement of β-phase precipitation during ageing heat treatment

As mentioned in Section 4.1, the increasing hardness during aging heat treatment at 773 K results from β-phase precipitation in the α (or Widmanstätten α) matrix. To confirm this and to explore it kinetically, hot-stage *in situ* X-ray diffractometry was carried out.

As indicated in Fig. 8, a peak at 54° corresponding to the β-phase appears in the diffraction pattern taken after 5 h aging. This is further important and direct evidence of the β-phase precipitation in the α matrix during aging heat treatment at 773 K.

The strength of the β diffraction seems to be saturated in a couple of hours. This indicates that the phase equilibrium is reached and the volume ratio of both phases is balanced in 6–7 h at this temperature.

Assuming this is reasonable, the precipitation of β-phase might finish after this time and only coarsening of β may continue after that. The coarsening of precipitates would result in a decrease in hardness. The hardness decrease in Fig. 4 on aging for 10–24 h, can be explained by this precipitate coarsening.

5. Conclusion

A Ti–Zr based alloy containing a few per cent of niobium as a β-stabilizing ternary element was developed in this study for use in biomedical applications. To obtain desirable mechanical properties, phase control by aging heat treatment was conducted and the relation between the phase constitution and mechanical properties was examined.

Altering the heat treatment of these alloys was found to be critical. Using a heat-treatment regime with aging at 773 K for 10 h produced the greatest increase in hardness for all niobium concentrations. Aging at 1073 K did not produce the same effect. This can be explained by considering the ternary phase diagram where at 773 K both the α and β phases are present. The precipitation process of β in the α matrix during aging at 773 K was confirmed through conventional X-ray diffractometry and *in situ* X-ray analysis using a hot stage mounted on the diffractometer.

The ternary alloys containing 1%–2% niobium have been shown to have potential as new biomedical alloys, when they have been heat treated under suitable conditions.

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