Quantum parameters for guiding the design of Ti-alloys with shape memory and/or low elastic modulus

Milena Arciniegas, Javier Peña, Jose Maria Manero, Juan Carlos Paniagua,
Javier Gil Mur

► To cite this version:

Milena Arciniegas, Javier Peña, Jose Maria Manero, Juan Carlos Paniagua, Javier Gil Mur. Quantum parameters for guiding the design of Ti-alloys with shape memory and/or low elastic modulus. Philosophical Magazine, 2008, 88 (17), pp.2529-2548. 10.1080/14786430802375667 . hal-00513950

HAL Id: hal-00513950

<https://hal.science/hal-00513950>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Quantum parameters for guiding the design of Ti-alloys with shape memory and/or low elastic modulus

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-08-Jul-0255
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	18-Jul-2008
Complete List of Authors:	Arciniegas, Milena; Technical University of Catalonia, Department of Materials Science and Metallurgy Peña, Javier; Technical University of Catalonia, Department of Materials Science and Metallurgy; Escola Superior en Disseny ELISAVA, Department of Materials Science Manero, Jose Maria; Technical University of Catalonia, Department of Materials Science and Metallurgy Paniagua, Juan Carlos; University of Barcelona, Department of Physical Chemistry Gil Mur, Javier; Technical University of Catalonia, Department of Materials Science and Metallurgy
Keywords:	density-functional theory, shape memory alloys, titanium alloys
Keywords (user supplied):	low elastic modulus

Quantum parameters for guiding the design of Ti-alloys with shape memory and/or low elastic modulus

M. Arciniegas^{1*}, J. Peña^{1,2}, J. M. Manero¹, J. C. Paniagua³ and F. J. Gil¹

^{1*}To whom correspondence should be addressed: Biomaterials and Biomechanics division, Department of Materials Science and Metallurgy, Technical University of Catalonia (UPC). Avda. Diagonal 647, Barcelona, 08028, Spain. Tel: +34-934-054-452, Fax: +34-934-016-706. Email: milena.arciniegas@upc.edu.

²Department of Materials Science. Escola Superior en Disseny ELISAVA. C/Ample 11-13, 08002 Barcelona, Spain.

³Department of Physical Chemistry, University of Barcelona. Martí i Franqués 1, 08028. Barcelona, Spain.

Abstract

Electronic structure calculations based on density functional theory have been applied to clusters of titanium with different alloying elements in order to obtain quantum parameters that give some information on the interaction between the mother and alloying atoms. Average values of these parameters weighted with the molar fractions have been calculated for 146 titanium alloys that exhibit shape memory and/or low elastic modulus. These values have been mapped in order to identify zones that group the alloys with either property. This information has been used as a guide for designing seven new alloys with desired properties. These have been microstructurally and mechanically characterized, and the results confirm the usefulness of the method.

Keywords: titanium alloys, shape memory alloys, low elastic modulus, density functional theory.

1. Introduction

Since 1963, when the shape memory effect was discovered on Ti-Ni alloys, different properties have been studied on the basis of the reversible phase transformation austenite-martensite caused by temperature change or stress applied on the material [1-4]. These include superelasticity, simple and double shape memory effects, high damping and outstanding wear behaviour. Advantages from these interesting properties have been taken in biomedical applications, for example osteosynthesis plates, jaw plates, orthodontic archwires, stents and dental implants [5-7]. The shape memory together with the high corrosion resistance and excellent biocompatibility of Ti give a good fulfilment of the strict requirements of such applications [8-10]. Several studies have been published about mechanical and biological properties of TiNi and the relationship between them [1,8]. Some controversy exists on the risk of Ni ions release from the implant to the surrounding tissue, which can produce adverse reactions [11-13]. Two ways of overcoming this problem have been proposed: surface modification by means of surface coating oxidation [14,15] and substitution of Ni by biocompatible and non-citotoxics alloying elements that preserve the excellent shape memory properties of Ti-Ni alloys [16-18].

Another aspect frequently reported in the literature is the stress-shielding effect caused by mechanical non-compatibility between bone and implant; a too stiff material absorbs the load and hinders bone regeneration [7,11]. Different Ti alloys have been studied for reducing the elastic modulus of implant material so as to favour bone regeneration. The most common approach consists in using non-toxic β -stabilizing alloying elements, such as Ta, Nb, Mo, Hf and sometimes also Zr, because the β -phase Ti alloys show lower

elastic modulus compared to the α -phase ones [19-20]. In order to guide the design of such alloys some researchers [21-23] have used a method based on molecular orbital theory, which was introduced by Morinaga and co-workers in 1988 [24, 25]. The aim of this method is to calculate quantum parameters that take into consideration the alloying element effect for predicting the stable phase of Ti-alloys. The parameters chosen by those authors the average bond order between the alloying and mother atoms and the mean energy of virtual d -orbitals centred upon the alloying element. A recently published article analyses the relationship of elastic properties with those parameters for a set of twenty alloys [26].

With these precedents in mind, we have done a review of works published from 1970 up to 2007, with the purpose of setting up a data base of Ti-alloys with low elastic modulus and/or shape memory effect. This data base collects 146 alloys and includes their heat and mechanical treatment, phase, elastic modulus and martensite start temperature (M_s temperature). In an attempt of improving the theoretical method for designing Ti alloys with the desired properties, a new set of parameters has been calculated by using a more modern quantum methodology, based on the Density Functional Theory. The application of the resulting parameters to the alloy data base has permitted to build a new map in which zones can be delimited for the alloys with shape memory and/or low elastic modulus. Although most of the alloys on the data base are biocompatible, some alloying elements with controversial biocompatibility behaviour, such as Fe, Al, V or Ni –the latter two under discussions [21] – have also been included for aiding to delimit the zones.

The new map has been used as a guide to design seven new alloys with low elastic modulus and/or memory shape. These have been microstructurally and mechanically characterized for measuring the elastic modulus and verifying the presence of thermoelastic martensite phase transformation induced by temperature, but also by stress under indentation conditions. Phase transformations can be evidenced on the load vs. displacement into surface ($P-h$) curves as events on the loading and unloading portions, such as pop-in, pop-out or hysteresis loops produced between load and reload cycles [27]. These latter have been well reported by V. Domnich and G. Gogotsi in other transforming materials, such as silicon, gallium arsenide and zirconium oxide [28], by X.G. Ma *et al.* [29] in TiNi shape memory thin films and by C.P. Frick *et al.* [30] in nickel-titanium sub-micron compression pillars.

2. Map generation

2.1 Calculation of the new parameter set

The parameters proposed by Morinaga and co-workers for charting the alloys are averages of the bond order between the alloying and mother elements (Bo) and of the mean energy of the lowest virtual d -orbitals of symmetry t_{2g} and e_g centred upon the alloying element (Md). These averages are weighted with the atomic fraction of each alloying element (x_i) [24]:

$$\overline{Bo} = \sum_{i=1}^{i=n} x_i \cdot Bo_i \quad (\text{Eqn. 1})$$

$$\overline{Md} = \sum_{i=1}^{i=n} x_i \cdot Md_i \quad (\text{Eqn. 2})$$

where n is the number of alloying elements in the alloy.

A cluster of 14 mother atoms surrounding one alloying atom with bcc structure was adopted for calculating the values of Bo_i and Md_i for each alloying element, and the Discret Variational $X\alpha$ (DV- $X\alpha$) method was used as computational tool [31]. It is assumed that Bo_i provides some measure of the strength of the bond between the alloying and mother elements, and Md_i correlates with the electronegativity and metallic radius of the alloying atom.

In the present work a new set of parameters has been calculated by using the Khon-Sham implementation of Density Functional Theory (DFT) with the hybrid exchange-correlation functional B3LYP [32,33]. DFT electronic structure calculations have proven a great success in obtaining properties of molecules and solids, and it is now well established as a useful tool for research in material science [34]. Over other electronic structure calculation methods of comparable accuracy it has the advantage of being conceptually simpler and very efficient from the computational point of view. The effect of internal electrons has been taken into account by means of the effective core potentials proposed by Hay and Wadt [35-37], that include some relativistic effects. The basis set used is the split-valence one put forward by Dunning *et al.* [38]. All the calculations have been done with the Gaussian package [39].

As in Morinagas's approach, a cluster of 14 mother atoms surrounding one alloying atom with bcc structure has been adopted to model the alloy. Cluster models have been used to model a wide variety of bulk properties of solids atoms [40], and they are considered a complement to band theory especially useful for studying local properties, as is the case

for the interaction of an alloying atom with the surrounding mother. Although the calculation results are dependent on the geometry of the cluster, the resulting differences can be overlooked, given the crude character of the parameters to be obtained [24]. While Morinaga used the energy of virtual d -orbitals to obtain one of the parameters, we have referred to referred it to the energy of occupied orbitals centered upon the alloying element. These are more localized and more basis set independent than the virtual ones, which usually have energies rather dependent on the basis set choice. On the other hand, their changed-sign energies provide good approximations to the corresponding ionization potentials [41,42]. These, in turn, are related to the Mulliken electronegativity, which is defined as the mean of the ionization potential and the electron affinity of the system. For each cluster we have carefully investigated different orbital occupations and spin multiplicities in order to find the ground electronic state. Then we have selected the highest occupied molecular orbital centered upon the alloying atom (HOMOAL), its absolute-value energy (OE) being a measure of the ionization potential of that atom in the cluster. The bond orders between the alloy and mother elements (BO) have been calculated by a natural poblational analysis (atom-atom overlap-weighted natural atomic orbital bond order, see [43]). This definition produces bond orders that are little dependent on the basis set choice, if minimal bases are not taken in account [44-45].

The BO and OE parameters obtained for the elements of the studied alloys are listed in Table 1, together with the values previously obtained by Morinaga and co-workers. It should be pointed out that OE values are expressed in atomic energy unities (hartrees), while Md values are reported in electron-volts. To obtain the weighted average values of

these parameters for each alloy expressions analogous to equations (1) and (2) have been used. The data of table 1 disclose that Md values calculated by Morinaga and the OE values calculated in the present work do not have a parallel behaviour. As already stated, Morinaga orbital energies are obtained from virtual orbitals obtained with DV- $X\alpha$ type calculations. These bear some inverse relationship to electron affinities: the more positive the energy the lower the electron affinity. On the other hand, our OE parameters are occupied orbital energies resulting from DFT-B3LYT calculations that include relativistic corrections, with the sign inverted in order to obtain positive numbers. Larger values of this parameter correlate with larger ionization potentials. Since both, the electron affinity and the ionization potential, contribute to Mulliken electronegativity one could expect an inverse relationship between Md and BO ; however, Md is based on d orbitals while OE refers to the HOMOAL, which have different degrees of s , p or d character depending on the system. Therefore, no direct connection exists between both parameters.

2.2 Ti-alloy data compilation

Table 2 collects 139 Ti-alloys reported on literature from 1970 to 2007 together with seven alloys fabricated in our laboratory, completing a total of 146. All of the compiled alloys present shape memory and/or are low elastic modulus according to the criterion of their respective authors. Other significant data, such as the publication year, the heat and/or mechanical treatments, the resulting phase, and the chemical composition, are also included in the table. After a peak in 1994, the publication rhythm is, in the average, approximately steady (see Fig.1). In some alloys with high β -stabilizing element content

some proportion of ω -phase is observed, as happens to those with numbers 1, 68-72, 113-117. The ω -phase may be suppressed by addition of some α -stabilizer, as Al (see the alloys 51a and 88), as well as by changing the heat treatment conditions (see the alloys 51b). Since the treatment influences the mechanical properties of the resulting material, some alloys have more than one entry in the table, these being distinguished by adding a letter to the alloy number (see, among others, the alloys numbered as 51-55 and 90). In a few instances duplicity of data comes from different references reporting on the same alloy.

The usual criterion for an alloy to be considered of low elastic modulus (LEM) has changed somewhat along the time: until the nineties elastic modulus values under 125 GPa were usually considered low, while this threshold has lowered to about 90 in the last years. Around 50% of the compiled alloys have an elastic modulus lower than this latter value. β -phase alloys have, in general, lower elastic modulus than the α -phase ones, which explains the high proportion of alloys with β -phase appearing in the table. Some heat treatments –such as annealing and aging– tend to increase the elastic modulus, thus explaining that of some of the β -phase alloys have relatively high values of that parameter. This is the case of the alloys 33b (102 GPa), 35 (112 GPa) and 52b (113 GPa). On the other hand, if the cooling rate is increased –using, for example, quench treatments in ice-water– the β -phase is favoured and the elastic modulus is significantly reduced. This reduction is particularly noticeable for some cold worked alloys such as 54a (50 GPa) and 90d (44 GPa).

About one third of the alloys display shape memory effect (SME); however, this proportion is not very meaningful, because many of the references do not mention this aspect. Shape memory is usually reported by the presence of thermoelastic martensitic plates induced by stress, but some of the articles only mention the martensite start temperature (M_s).

A relevant number of the compiled alloys have been developed for being used in the biomedical field. Low elastic modulus is a frequent requisite in this field; which explains that the most common alloying elements are the highly biocompatible β -stabilizers Ta, Nb and Mo [9]. Shape memory is also a desired property for some biomedical applications such as cardiovascular stents, orthodontic wires and orthopedic plates. The fact that some alloys exhibit both properties (see, for instance, 55, 56, 88, 110, 130 and 134) opens interesting possibilities not yet fully exploited such as their service in load-transfer devices.

2.3. Alloy charts

The calculated BO and OE parameters (Table 1) have been used together with the chemical compositions listed in the Table 2 to obtain, for each alloy, average values, $\overline{BO}$ and $\overline{OE}$, weighted with the molar fractions. These have been plotted in a two-dimensional graph with different symbols for indicating the phase and the LEM and/or SME properties (Fig. 2). The α and β phases are identified by a black star and a grey circle, respectively, while a grey triangle indicates the coexistence of both phases. Although a few alloys show a small proportion of a third ω -phase, these have been identified according to the predominant phase. A hollow symbol indicates LEM, and a

1
2
3 multiplication sign is used for SME. These two symbols are superimposed when both
4 properties are present. For an alloy to be considered of low elastic modulus we have
5 adopted the more restrictive criterion based on a 90 GPa threshold. The equiatomic TiNi
6 alloy (number 56), which presents $\overline{BO}$ and $\overline{OE}$ values very different from those of the rest
7 of the alloys, has not been included in the diagram, so as to get a better differentiation of
8 the other points.
9

10
11 The α phase alloys appear at the right side of the map, while β alloys are mostly on the
12 left hand side. Those in which both phases coexist extent from the middle to the right
13 side. In fact, the presence of both phases indicates that the heat-mechanical treatment has
14 not lead to a complete transformation to the more stable phase. We have drawn a solid
15 line and a dotted one that enclose the alloys with LEM and those with SME, respectively.
16 The zones corresponding to these two properties are mostly on the left side of the map.
17 This agrees with the fact that α stabilizers tend to increase the elastic modulus. LEM
18 predominate in the upper part and SME in the lower side. Both zones overlap in a region
19 including the alloys for with both properties have been reported.
20

21
22 It should be noted that the drawn lines do not represent sharp frontiers, since each region
23 includes some alloys not bearing the corresponding property. This is due, on the one
24 hand, to the fact that the calculated parameters only provide a crude representation of the
25 structural features determining LEM and SME, and, on the other, to the mechanical
26 properties depending on the heat treatment applied to the alloy, which cannot be taken
27 into account in such a kind of maps. One should also take into consideration that in many
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

of the compiled works only one of those two properties has been studied, so that there surely are more alloys with one or the other property than indicated. Thus, the drawn frontiers are rather speculative, and should be reconsidered in the light of future experimental information. Nevertheless, they provide valuable information on where to look for alloys with desired properties, as we will later show.

For the sake of comparison we have also used Morinaga's parametrization to calculate the *Bo* and *Md* values of the alloys collected in table 2, except for those containing the elements oxygen (alloy 67) and gallium (alloys 92 and 93), which were not included in the published list of parameters. The results have been plotted in Fig. 3 using the same symbols as in Fig. 2, and zones enclosing the alloys with LEM and SME have been delimited with the same criterion as in that figure. The first thing to note is that both maps have a very different aspect, which is due to the arguments already mentioned while discussing the data of Table 1: different quantum calculation method, bond order definition and type of chosen orbital, and inclusion of relativistic corrections in the pseudopotentials used for the present calculations, which can be relevant for atoms with high atomic number. This is the case of some alloying elements that are particularly useful for biomedical applications: Nb, Ta, Zr and Hf. In Fig. 3 most of the LEM zone is included into the SME region, and the alloys with one or the other property appear rather mixed, especially in the upper part of the diagram. In fact, Morinaga's parametrization was not initially intended to represent those properties, but rather to differentiate phases and deformation mechanisms (slip and twin), as well as to identify alloys that lead to martensite on quenching. The zones corresponding to LEM and SME are more separated

in the map of Fig. 2, and they overlap in a smaller region with a high proportion of alloys bearing both properties.

3. Design of seven new alloys

Many alloys with excellent mechanical properties for biomedical applications contain Ni in their composition (see, for instance, the Ti-Ni-Cu-Mo alloys with numbers 84 to 87 and the Ti-Ni-Ta ones numbered 124, 125 and 126). However, the fact that the atoms of this element released from an implant can produce adverse reactions has motivated the search of new, Ni-free formulas for substituting those alloys. The above presented map has been used to guide the design of seven new alloys, which are expected to show low elastic modulus and/or shape memory. They are numbered consecutively from 128 to 134 in table 2, and their $\overline{OE}$ and $\overline{BO}$ coordinates are (0.1526, 0.6089) for the alloy numbered 128, (0.1530, 0.6079) for 129, (0.1540, 0.6054) for 130, (0.1524, 0.6101) for 131, (0.1535, 0.6119) for 132, (0.1542, 0.6107) for 133 and (0.1533, 0.6070) for 134. The one numbered 131 is clearly located in the LEM zone, at the left side of the map. Those with numbers 128, 130, 132 and 133 are situated in the LEM zone near the boundary of the SME region, and the measurement of their properties has permitted to better define that boundary. The two remaining alloys (129 and 134) were chosen well inside the overlap area.

3.1. Experimental procedure

The alloys were fabricated using an electric arc furnace in controlled Ar atmosphere, cast in 40 g buttons from bars of the starting elements of 99.9% purity. The buttons were

1
2
3 melted five times for enhancing the material homogenization and avoiding segregation of
4 the heavier elements. Then, buttons were encapsulated within a vacuum quartz tube,
5
6 solution treated at 1100°C for 1.5 hours and quenched in ice-water. Samples of both
7
8 alloys were mounted on Bakelite, mechanically polished and finished with colloidal silica
9
10 to give a average surface roughness of <100nm for using in the different characterization
11
12 techniques. A Fischerscope X-ray System HDL equipment was used for verifying the
13
14 chemical composition. The tests were conducted on four different positions –from centre
15
16 to periphery– of each sample for evaluating the chemical homogeneity. The samples were
17
18 etched with Keller reactive (2 ml HF, 3ml HCl, 5 ml HNO₃ and 190 ml H₂O) for optical
19
20 microstructural analysis. A differential scanning calorimeter (DSC) Q1000 TA
21
22 Instrument was used for determining the presence of thermoelastic phase transformation
23
24 and its corresponding temperatures. With the purpose to remove the thermal and
25
26 mechanical history on the alloys, which could modify the phase transformation
27
28 temperatures, 2 cycles of heating and cooling were applied from -90°C to 200°C. Then,
29
30 only the second cycle was used for determining the transformation temperatures by
31
32 means of the line intercept method. Rectangular plates of 10 x 10 x 25 mm were
33
34 machined, ground, and polished after heat treatment for measuring the elastic modulus by
35
36 ultrasounds transmission method at room temperature using a USN50 ultrasound
37
38 instrument. The tests were conducted by means of transmitters of longitudinal and
39
40 transversal waves, which were coupled on the specimen surface. A coupling-solution was
41
42 employed in order to improve the wave propagation. The elastic modulus was calculated
43
44 by means of the Eqn. 3 and 4.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

$$\nu = 1 - \frac{1}{2} \cdot \frac{1}{1 - \left(\frac{C_t}{C_l}\right)^2} \quad (\text{Eqn. 3})$$

$$E = 2 \cdot \rho \cdot (1 + \nu) \cdot C_t^2 \quad (\text{Eqn. 4})$$

where C_t and C_l are the transversal and longitudinal wave velocities, respectively, ν is the Poisson coefficient and ρ is the alloy density. The error was 5% approximately, estimated from the error in specimen dimension generated by polishing.

Finally, on each sample of the studied alloys fifteen cyclic instrumented indentation tests were performed, in which the load was linearly increased up to the maximum of 625 mN, using an MTS System Nano Indenter XP. The tests were carried out using a spherical tip with a radius of 750 nm in order to evaluate the phase transformation induced by stress in the new alloys under indentation loading. All tests were conducted at room temperature and started when the thermal drift was maintained lower than 0.05 nms^{-1} . The thermal drift was estimated and corrected during the test automatically. A strain rate of 0.05 s^{-1} was applied in loading, unloading and reloading. In order to guarantee the contact throughout the test, the indenter was unloaded after every cycle up to 95% of the maximum load applied in the cycle.

3.2 Microstructure, physics and mechanical properties of the new alloys

The relevant properties of the seven new alloys are collected in Table 3. Only a wt % variation of alloying element lower to 1% was estimated between the theoretical chemical composition and those determined by x-ray fluorescence. No significant differences were

found between centre and periphery of the samples, which indicates a good homogenization of the studied alloys in the established composition.

Fig. 4 shows representative optical micrographs for the different microstructures of the studied alloys: β -prior grains homogenously distributed on the samples of the new alloys numbered as 128, 131 and 132 (see Fig. 4a from the alloy numbered as 131), β -prior grains accompanied by acicular and short plates on the alloys numbered as 129 and 133 (see Fig. 4b from the alloy numbered as 129), and acicular and fine plates of different sizes within β -prior grains on the alloys numbered 130 and 134 (see Fig. 4c from the alloy numbered as 134). X-ray diffraction profiles of the new alloys, shown in Fig. 5, confirmed the presence of the β -phase, especially in the alloys numbered as 128, 131 and 132, associated to the (002), (200) and (211) diffraction planes. Also, the α'' -phase was detected in the rest of the new alloys, particularly in the alloys numbered as 130 and 134, in which a characteristic double pick of this phase, around 40° of theta angle, was observed on the x-ray profiles. These results are in agreement with the predictions from the maps (see Fig. 2) and confirm the relation between β -stabilizer content and amount of α'' -martensite plates: an increment of β -stabilizer content decreases the α'' -phase fraction by hindering the α'' plates nucleation [70].

In order to evidence the temperature-induced thermoelastic martensitic phase transformation that can taken place, the new alloys were analysed by DSC. Reversible changes of thermodynamic baseline associated to the one-step reversible phase

transformation from austenite to martensite on heating and cooling [1-3], with an M_s temperatures of 125°C and 45°C, for the Ti-13.7Nb-1.4Ta (130) and Ti-19.1Nb-8.8Zr (134) alloys, respectively, were appreciated on the DSC profiles, whereas the rest of the alloys did not evidence any martensitic transformation (see Fig. 6 in which the DSC plot obtained from the alloy 134 in contrast with that obtained from the alloy 131 are shown). Contrarily to what was expected by the authors, the new alloys numbered as 129 and 130 did not present temperature induced reversible phase transformation, although they were designed inside of the SME zone (see Fig. 2) and presented α'' -thermoelastic martensite phase, detected by x-ray diffraction. This can be explained by a low fraction of α'' -phase, which restraints the transformation capability or a transformation temperature out of the testing conditions.

According with the results of the ultrasound tests, the alloys object of this study show elastic moduli values in a range from 67 to 79 GPa. As predicted by the design method, all values are relatively low compared with alloys currently employed in the biomedical field.

Finally, with the purpose to evidence the stress-induced thermoelastic martensitic phase transformation (TPT) the new alloys were subjected to indentation tests. Thin and well defined hysteresis loops produced between load and reload cycles were observed in all the P-h curves obtained from the alloys numbered as 128, 129, 130 and 134 (see Fig. 6 in which one representative P-h curve of the alloys numbered as 128 is shown in solid line), whereas the rest of the alloys no changes in the P-h curves were appreciated (see Fig. 6 in

which one representative P-h curve of the alloys numbered as 132 is shown in dashed line). Such difference between the unloading and reloading path is explained by the fact that in transforming materials, when load is released, both the elastic response (prevalent in the beginning) and the phase transformation in the form of continuous reverse twinning (when the stress decreases below the critical stress for transformation) contribute to the recovery, and during the successive reloading a different stress state activates again the transformation, which generates the observed loops. Similar behaviour have been reported in other type of transforming materials [71] and by C.P Frick *et al.* [30,72] on TiNi alloys at very low indentation depth and also evidenced under cyclic uniaxial tests of shape memory alloys [73,74]. Conversely, in cyclic loading of non-transforming materials, the unloading portion of a *P-h* curve is completely elastic and the subsequent reloading follows the same path. In order to confirm that such differences between unloading and reloading path are due to the presence of induced-stress phase transformation, the P-h curves obtained were analyzed using the power law relation proposed by W.C. Oliver *et al.* [75], which shows that during elastic unloading and reloading, the relation between load (P) and displacement into surface (h) is given by:

$$P \propto (h - h_f)^{1.5} \quad (\text{Eqn. 5})$$

Accordingly, the material is reloaded elastically until the maximum load of the previous cycle is reached, thereafter plastic deformation is resumed. In our transforming materials, strong deviation from such relation was manifested, confirming that the response is due not only to elastic recovery, but also to phase transformation. Non-transforming materials, conversely, showed good agreement with the mentioned law.

The alloys 128, 129, 130 and 134 are especially interesting because they combine a rather low elastic modulus with shape memory effect; in particular, the latter two, that exhibit a change of phase activated by temperature variation. The transformation temperature could be modified through mechanical and/or heat treatment so as to conform to the needs of certain biomedical applications.

4. Conclusions

Theoretical parameters have been calculated by applying density functional theory to clusters of 14 titanium atoms surrounding different alloying central elements in order to model the interaction between Ti and the alloying atom. A compilation of data on 146 Ti-alloys with shape memory and/or low elastic modulus has permitted to characterize each alloy with averages of those parameters weighted with the molar fraction of its components, and these data have been used to draw a map where regions corresponding to those two properties can be delimited. This map has been used as a guide for searching new alloys with good qualities for medical use. Seven new alloys have been designed and microstructurally and mechanically characterized. As expected from the map, all of them present low elastic modulus, and some of them also have memory shape, which has been used for better defining the boundary of the corresponding zone. Two of them present martensite phase transformation thermally induced with M_s temperatures of 125°C and 45°C respectively, which could be modified through mechanical and/or heat treatment for applications that require a transformation at body temperature. Other two alloys show stress-induced phase transformation under cyclic nanoindentation conditions.

These results confirm the usefulness of the proposed methodology for guiding the search of alloys with LEM and/or SME.

Acknowledgements

The authors wish to thank Spanish Ministry of Science and Technology for financial support through grants MAT2005-07244-C03-01, CTQ2005-08459-CO2-01 and BIO2004-05436. They also want to acknowledge the referees for useful comments.

References

[1] T.W. Duering, A.R. Pelton. Ti-Ni Shape Memory Alloys. In: R. Boyer, G. Welsch, E.W. Collings, editors. *Materials Properties Handbook Titanium Alloys*, ASM International, 1994. p.1035.

[2] T.W. Duering, K.N. Melton, C.M. Wayman. *Engineering aspects of shape memory alloys*. Ed. Butterworth-Heinemann Ltd., 1990.p.3

[3] B.G. Mellor. Martensitic transformation and the shape memory effect. In: *Science and technology of shape memory alloys*. Ed. V. Torra, 1987, p.274.

[4] E. Hornbogen: *Prakt. Metallogr.* (Germany), 1989, vol. 26, p. 279.

[5] K. Wang. *Mater. Sci. Eng. A*, 213, 1996, 134-137.

[6] M. Long, H.J. Rack. *Biomaterials*, 19, 1998, 1621-1639.

[7] M. Niinomi. *Sci. Technol. Adv. Mater.*, 4, 2003, 445-454.

[8] S.G. Steinemann. *Surface performance of Titanium*. Warrendale, PA:TMS33-45, 1996.

[9] Y.Okazaki, Y. Ito, K. Kyo, T. Tateisi. *Mater. Sci. Eng. A*213, 1996, 138-147.

- [10] S.A. Shabalovskaya. *Intern. Mat. Review.* 46, 2001, 233-250.
- [11] M. Niinomi. *Metall. Mater. Trans. A*, 32, 2001, 477-486.
- [12] M. Niinomi. *JOM.*, 51, 1999, 32-34.
- [13] K. Wang. *Mater. Sci. Eng. A*, 213, 1996, 134-137.
- [14] A. Michiardi, C. Aparicio, J.A. Planell, F.J. Gil. *J. Biomed. Mater. Res. Part B: Appl Biomater.*, 77B, 2006, 249-256.
- [15] S.A. Shabalovskaya. *Bio-med. Mat. Eng.* 6, 1996, 267-289.
- [16] Y. Fukui, T. Inamura, H. Hosoda, K. Wakashima, S. Miyasaki. *Mater. Trans.*, 45, 2004, 1077-1082.
- [17] J.-P. Noh, D.-W. Chung, H.-W. Lee, T.-H. Nam. *Mater. Sci. Technol.*, 17, 2001, 1544-1550.
- [18] T. Grosdidier, M. J. Philippe. *Mater. Sci. Eng. A.*, 291, 2000, 218-223.
- [19] Y. Okasaki. *Curr. Opin. Solid State Mater. Sci.*, 5, 2001, 45-53.
- [20] Y.H. Hon, J.Y. Wang, Y.N. Pan. *Mater. Lett.*, 58, 2004, 3182-3186.
- [21] D. Kuroda, M. Niinomi, M. Morinaga, Y. Kato, T. Yashiro. *Mater. Sci. Eng.* 243, 1998, 244-249.
- [22] M. Morinaga, M. Yoshinori, Y. Hisoshi. *Mater. Sci. For.*, 449, 2004, 37-42.
- [23] Saito T. et.al. *Science*, 300, 2003, 464-467.
- [24] M. Morinaga, M. Kato, T. Kamimura, M. Fukumoto, I. Harada, K. Kubo. In: *Sixth World Conference on Titanium*. Francia, vol. 1, 1988, p. 1601.
- [25] M. Morinaga, N. Yukawa. In: *Computer Aided Innovation of New Materials*. Japon, 1991, p. 803.
- [26] H. Adachi, M. Tsukada, C. Sakoto. *J. Phys. Soc. Japan* 45, 1978, 875-883.

- [27] M. Arciniegas, J.M. Manero, J. Peña, F.J. Gil, J.A. Planell. *Met. Mater. Trans. A*, 39, 2008, 742-751.
- [28] V. Domnich, Y. Gogotsi. Phase transformation in silicon under contact loading. *Rev. Adv. Mater. Scie.*, 3, 2002, 1-36.
- [29] X.G. Ma, K. Komvopoulos. In situ transmission electron microscopy and nanoindentation studies of phase transformation and pseudoelasticity of shape-memory titanium-nickel films. *J. Mater. Res.*, 20, 2005, 1808-1813.
- [30] C.P. Frick, S. Orso, E. Arzt. Loss of pseudoelasticity in nickel–titanium sub-micron compression pillars. *Acta Mater.*, 55, 2007, 3845-3855.
- [31] M. Abdel-Hady, K. Hinoshita, M. Morinaga. *Scripta Mater.* 55, 2006, 477-480.
- [32] A. D. Becke. *J. Chem. Phys.* 98, 1993, 5648.
- [33] C. Lee, W. Yang, R. G. Parr. *Phys. Rev. B* 37, 1988, 785.
- [34] W. Koch, M. C. Holthausen. *A Chemist's Guide to Density Functional Theory*, 2nd ed., Wiley-VHC, Weinheim, 2001.
- [35] P. J. Hay, W. R. Wadt. *J. Chem. Phys.* 82, 1985, 270.
- [36] W. R. Wadt, P. J. Hay. *J. Chem. Phys.* 82, 1985, 284
- [37] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* 82, 1985, 299.
- [38] T. H. Dunning Jr. and P. Hay. In: *Modern Theoretical Chemistry*. Ed. H. F. Schaefer III, 3, 1. New York, 1976.
- [39] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K.

- Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [40] G. Pacchioni, P. S. Bagus and F. Parmigiani, Cluster Models for Surface and Bulk Phenomena, NATO ASI Series, Series B: Physics Vol. 283, Plenum Press, New York, 1992.
- [41] D. P. Chong, O. V. Gritsenko, E. J. Baerends, J. of Chem. Phys. 116, 1760-1772, 2002.
- [42] S. Hamel, P. Duffy, M. E. Casida, D. R. Salahub, J. Electron Spectrosc. Relat. Phenom. 123, 345-363, 2002.
- [43] J. E. Carpenter, F. Weinhold, J. Mol. Struct. (Theochem.) 169, 41, 1988.
- [44] A. E. Reed, F. A. Weinhold, J. Chem. Phys. 78, 4066-4073, 1983.
- [45] A. E. Reed, R. B. Weinstock, F. A. Weinhold, J. Chem. Phys. 83, 735-746, 1985.
- [46] C. Baker. Metal Science Journal, 5, 1971, 92-100.

[47] H. Sasano, T. Suzuki. In: G. Lutjering, U. Zwicker and W. Bunk, Editors, Proceedings of the 5th International Conference on Titanium DGM, Weinheim (1985), p. 1667.

[48] R. Boyer, G. Welsch, E.W. Collings. Materials Properties Handbook: Titanium Alloys. ASM International, Materials Park, OH, USA, 1994.

[49] T. Grosdidier, M.J. Philippe. Mater. Sci. Eng. A., 291, (2000), p.218.

[50] C. Lei, M. Wu, L. McD. Schetky, C. Burstone. In: SMST-97- Proceedings of the Second International Conference on Shape Memory and Superelastic Technologies, (Eds. A. Pelton, et al.), Pacific Grove, California, USA, 1997, p.503.

[51] Y.Okasaki, S. Rao, Y. Ito, T. Tateisi. Biomaterials, 19, 1998, 1197-1215.

[52] J. Black, G. Hasting. Handbook of Biomaterials Properties. Chapman and Hall, editors. 1998.

[53] W.F. Ho, C.P. Ju, J.H. Chern Lin. Biomaterials, 20, 1999, 2115-2122.

[54] X. Tang, T. Ahmed, H.J. Rack. J. Mater. Sci., 35, 2000, 1805-1811.

[55] K. Nitta, S. Watanabe, N. Masahashi, H. Hosada, S.Hanawa. In: M. Niinomi, T. Okabe, E.M. Taleff, D.R. Lesuer, H.F. Lippard, editors, Structural Biomaterials for the 21st Century, TMS, 2001, 25-34.

[56] P. Olier, L. Chandrasekaran. Materiaux (France), 2002, 349-354.

[57] E. Takahashi, S. Watanabe, S. Hanada. In: The International Conference on Shape Memory and Superelastic Technologies, USA, 2003, p.91.

[58] H.Y. Kim, Y. Ohmatsu, J.I. Kim, H. Hosoda, S. Miyazaki. Mater. Trans. 45, 2004, 1090-1095.

[59] M. Ikeda, S-Y. Komatsu, Y. Nakamura. Mater. Trans. 43, 2002, 2984-2990.

- [60] T. Ozaki, H. Matsumoto, S. Watanabe, S. Hanada. *Mater. Trans.*, 45, 2004, 2776-2779.
- [61] R. Banerjee, S. Nag, J. Stechschulte, H.L. Fraser. *Biomaterials*, 25, 2004, 3413-3419.
- [62] Y.J. Hon, J.Y. Wang, R.R. Jeng, C.H. Yeh, Y.N. Pan. *Journal of Taiwan Foundry Society*, 30, 2004, 33-40.
- [63] N. Sakaguchi, M. Niimori, T. Akahori. *Mater. Trans.*, 45, 2004, 1113-1119.
- [64] T. Maeshima, M. Nishida. *Mater. Trans.* 45, (2004), 1096-1100.
- [65] J.I. Kim, H.Y. Kim, T. Inamura, H. Hosoda, S. Miyazaki. *Mater. Sci. Eng. A.*, 403, 2005, 334-339.
- [66] C.W. Gong, Y. N. Wang, D.Z. Yang, *Mater. Chem. Phys.*, 96, 2006, 183-187.
- [67] D.H. Ping, C.Y. Cui, F.X. Yin, Y. Yamabe-Mitarai. *Scripta Mater.*, 54, 2006, 1305-1310.
- [68] Y. Horiuchi, K. Nakayama, T. Inamura, H.Y. Kim, K. Wakashima, S. Miyazaki, H. Hosoda. *Mater. Trans.* 48, (2007), 414-421.
- [69] H.Y. Kim, N. Oshika, J.I. Kim, T. Inamura, H. Hosoda, S. Miyazaki. *Mater. Trans.* 48, (2007), 400-406.
- [70] Y.L. Hao, M. Niinomi, K. Fukunaga, Y.L. Zhou, R. Yang, A. Suzuki. *Metall. Mater. Trans.*, 33, 2002, 3137-3144.
- [71] Y.G. Gogotsi, V. Domnich. *J. Mater. Res.*, 15, 2000, 871-879.
- [72] C.P. Frick, T.W. Lang, K. Spark, K. Gall. *Acta. Mater.*, 54, 2006, 2223-2234
- [73] Y. Horiuchi, K. Nakayama, T. Inamura, H.Y. Kim, K. Wakashima, S. Miyazaki, H. Hosoda. *Mater. Trans.* 48, (2007), 414-421.

[74] Y. Horiuchi, T. Inamura, H.Y. Kim, K. Wakashima, S. Miyazaki, H. Hosoda.
Mater. Trans. 48, (2007), 407-413.

[75] W.C. Oliver, G.M. Pharr. J. Mater. Res., 19, no.1, 2004, 3-20.

Figure Legends

- Figure 1. Number of publications per year about low elastic modulus and shape memory alloys, from 1994 to 2008.
- Figure 2. Alloy chart based on the *OE* and *BO* parameters proposed in the present work (see table 1). The mapped alloys are those listed in table 2. The solid line encloses the alloys with LEM, and the dashed line those with SME.
- Figure 3. Alloy chart based on the *Md* and *Bo* parameters proposed by Morinaga and coworkers (see table 1). The mapped alloys are those listed in table 2, except for those containing O, Bi or Ga. The solid line encloses the alloys with LEM, and the dashed line those with SME.
- Figure 4. Optical micrographs show β -prior grains (a), β -prior grains and α'' -plates within them (b) and mainly α'' -phase (c) in the alloys 131, 129 and 134, respectively.
- Figure 5. X-ray diffraction patterns of the designed and fabricated alloys.
- Figure 6. DSC plots of the alloys 131 and 134 after heat treatment. The alloy number 134 presents an *Ms* temperature of 45°C and the alloy 131 did not evidenced thermoelastic martensite transformation.
- Figure 7. Nanoindentation load-displacement behaviour of the alloys 128, 130 and 131 obtained under cyclic increasing-load-control conditions. The rows mark the hysteresis between loading and unloading portions.

Number of publications per year about low elastic modulus and shape memory alloys, from 1994 to 2007.

83x60mm (600 x 600 DPI)

Alloy chart based on the OE and BO parameters proposed in the present work (see table 1). The mapped alloys are those listed in table 2. The solid line encloses the alloys with LEM, and the dashed line those with SME.

160x160mm (600 x 600 DPI)

Alloy chart based on the Md and Bo parameters proposed by Morinaga and coworkers (see table 1). The mapped alloys are those listed in table 2, except for those containing O, Bi or Ga. The solid line encloses the alloys with LEM, and the dashed line those with SME.

160x161mm (600 x 600 DPI)

Optical micrographs show β -prior grains (a), β -prior grains and α -plates within them (b) and mainly α -phase (c) in the alloys 131, 129 and 134, respectively.
83x55mm (300 x 300 DPI)

Optical micrographs show β -prior grains (a), β -prior grains and α -plates within them (b) and mainly α -phase (c) in the alloys 131, 129 and 134, respectively.
83x56mm (300 x 300 DPI)

Optical micrographs show β -prior grains (a), β -prior grains and α -plates within them (b) and mainly α -phase (c) in the alloys 131, 129 and 134, respectively.
83x56mm (300 x 300 DPI)

X-ray diffraction patterns of the designed and fabricated alloys.

66x52mm (600 x 600 DPI)

DSC plots of the alloys 131 and 134 after heat treatment. The alloy number 134 presents an M_s temperature of 45°C and the alloy 131 did not evidenced thermoelastic martensite transformation.
83x72mm (600 x 600 DPI)

Nanoindentation load-displacement behaviour of the alloys 128, 130 and 131 obtained under cyclic increasing-load-control conditions. The rows mark the hysteresis between loading and unloading portions.

83x60mm (600 x 600 DPI)

Table 1. Quantum parameters calculated in the present work and those proposed by M. Morinaga and co-workers [24,26].

Element	Values obtained in the present work		Values obtained by Morinaga and co-workers	
	<i>BO</i>	<i>OE/hartree</i>	<i>Bo</i>	<i>MD/eV</i>
O	0.0864	0.19248	-	-
Al	0.5277	0.16041	2.426	2.200
Si	0.5163	0.14593	2.561	2.200
Ti	0.6041	0.15454	2.790	2.447
V	0.6498	0.15438	2.805	1.872
Cr	0.6299	0.15445	2.779	1.478
Mn	0.5710	0.15305	2.723	1.194
Fe	0.4482	0.15270	2.651	0.969
Co	0.3856	0.15244	2.529	0.807
Ni	0.3368	0.15137	2.412	0.724
Cu	0.3083	0.14949	2.114	0.567
Ga	0.5227	0.11182	-	-
Ge	0.5009	0.15247	-	-
Zr	0.6827	0.17708	3.086	2.934
Nb	0.6207	0.14741	3.099	2.424
Mo	0.5768	0.14729	3.063	1.961
Pd	0.3601	0.14653	2.208	0.347
Ag	0.3288	0.14386	2.094	0.196
Sn	0.5182	0.14086	2.283	2.100
Hf	0.6698	0.14857	3.110	2.975
Ta	0.6229	0.14723	3.144	2.531
Pt	0.3685	0.14787	2.252	0.146
Au	0.2916	0.13708	1.953	0.258
Bi	0.5234	0.14607	-	-

Table 2. Shape memory and low elastic modulus Ti-alloys reported in literature from 1970 to 2007.

ST: solution treated; WQ: water quenching; An: annealing; Ag: aging; AC: air cooling; OQ: oil quenching; CW: cold working, Sr: sheet rolled, Hr: Hot rolled, Cd: cold drawing. Ms: martensitic start temperature; Tr: room temperature; SE: superelasticity; SME: shape memory effect.

N°	Year	Ref	Chemical composition (wt.%)	Conditions	Phase	E (GPa)	Ms (°C)
1	1970	46	Ti-35Nb	WQ,CW,An,WQ	$\beta+\alpha''+\omega$		$M_s < T_r$
2	1985	4	Ti-14Mo-3Al	ST, WQ	$\beta+\alpha''$		SME
3	1985	47	Ti-15Mo-3Al	ST, WQ	$\beta+\alpha''$		SME
4	1994	48	Ti-7Al-4Mo	ST,An	$\alpha+\beta$	111	
b	1994	48	Ti-7Al-4Mo	ST,Ag	$\alpha+\beta$	116	
5	1994	48	Ti-5Al-5Sn-2Zr-2Mo-2Cr-0.25Si	ST,An	$\alpha+\beta$	114	
6	1994	48	Ti-4Al-2Sn-4Mo	ST,Ag	$\alpha+\beta$	115	
7	1994	48	Ti-13V-11Cr-3Al	ST	β	101	
b	1994	48	Ti-13V-11Cr-3Al	ST,Ag	β	110	
8	1994	48	Ti-4Sn-6Zr-11.5Mo-0.35Fe	ST,An	β	103	
9	1994	48	Ti-8Al-1Mo-1V	Duplex An	α	120	
10	1994	48	Ti-5Al-2.5Sn	ST,An	α	110-125	
11	1994	48	Ti-11Sn-5Zr-2.25Al-1Mo-0.25Si	Duplex An	α	114	
12	1994	48	Ti-6Al-2Nb-1Ta-1Mo	Sr	α	114	
13	1994	48	Ti-6Al-5Zr-0.5Mo-0.25Si IMI 685	ST,OQ,Ag	α	125	
14	1994	48	Ti-5Al-2.5Fe	Sr	$\alpha+\beta$	110	
15	1994	48	Ti-6Al-2Sn-1.5Zr-1Mo-0.35Bi-0.1Si	ST,An	α		
16	1994	48	Ti-5.5Al-3.5Sn-3Zr-1Nb-0.3Mo-0.3Si	ST,An	α		
17	1994	48	Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si	ST,An	α		
18	1994	48	Ti-6Al-2Sn-4Zr-2Mo-0.08Si	ST,An	α	114	
19	1994	48	Ti-4Al-4Sn-4Mo-0.25Si	ST,An	$\alpha+\beta$		
20	1994	48	Ti-2Al-11Sn-4Zr-1Mo-0.25Si	ST,An	$\alpha+\beta$		
21	1994	48	Ti-6Al-5Zr-4Mo-1Cu-0.2Si	ST,An	$\alpha+\beta$		
22	1994	48	Ti-6Al-2Sn-4Zr-6Mo	ST,An	$\alpha+\beta$	114	
23	1994	48	Ti-3Al-2.5V	St,An	α	105	
24	1994	48	Ti-6Al-1.65Fe	An	$\alpha+\beta$	127	
25	1994	48	Ti-8Mo	ST,An	$\alpha+\beta$	113	
26	1994	48	Ti-6Al-6V-2Sn	ST,An	$\alpha+\beta$	110	
27	1994	48	Ti-4Al-3Mo-1V	ST,Ag	$\alpha+\beta$	117	
28	1994	48	Ti-4.5Al-3V-2Mo-2Fe	An	$\alpha+\beta$	110	
29	1994	48	Ti-4.5Al-5Mo-1.5Cr	An	$\alpha+\beta$	114	
30	1994	48	Ti-5Al-1.5Fe-1.4Cr-1.2Mo	An	$\alpha+\beta$	114	
31	1994	48	Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si	An	$\alpha+\beta$	114	
32	1994	48	Ti-15Mo-3Al-2.7Nb-0.25Si	ST, An,Ag	β	97	

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

			TIMETAL 21S				
b	1997	6	Ti-15Mo-3Al-2.7Nb-0.25Si TIMETAL 21S	ST,An	β	74	
33	1994	48	Ti-11.5Mo-6Zr-4.5Sn BETA III	ST,An	β	68	
b	1994	48	Ti-11.5Mo-6Zr-4.5Sn BETA III	ST,Ag	β	102	
34	1994	48	Ti-3Al-8V-6Cr-4Mo-4Zr BETA C	ST,An	β	80	
35	1994	48	Ti-10V-2Fe-3Al	ST,An	β	112	
36	1994	48	Ti-15V-3Al-3Cr-3Sn	ST	β	81	
37	1994	48	Ti- 5Al-2Sn-4Zr-4Mo-2Cr-1Fe	ST,Ag	$\alpha+\beta$	122	
b	2000	49	Ti- 5Al-2Sn-4Zr-4Mo-2Cr-1Fe	ST,WQ	$\beta+\alpha''$		SME
38	1994	48	Ti-8Mo-8V-2Fe-3Al	ST	β	70	
39	1994	48	Ti-6Al-7Nb	ST,An,AC	$\alpha+\beta$	105	
40	1996	5	Ti-12.5Nb-12.5Zr-0.25Fe	ST,Ag	β	82	
41	1996	5	Ti-12Mo-6Zr-2Fe (TMZF TM)	ST,WQ	β	74	
42	1996	5	Ti-16.5Nb-9.5Hf Tiadyne 1610	ST,Ag	β	81	
43	1996	5	Ti-15Mo-3Nb Timetal 21SRx	An	β	83	
44	1996	5	Ti-6Al-4V	ST,An	$\alpha+\beta$	110	
45	1996	5	Ti-15Mo	ST,An,WQ	β	78	
46	1997	50	Ti-11Mo-3Al-2V-4Nb	ST,WQ	$\beta+\alpha''$		SME
47	1998	51	Ti-6Al-6Nb-1Ta		$\alpha+\beta$		
48	1998	51	Ti-6Al-2Nb-1Ta		$\alpha+\beta$		
49	1998	51	Ti-15Sn		$\alpha+\beta$		
50	1998	51	Ti-15Zr		$\alpha+\beta$		
51	1998	6	Ti-15Mo-2.8Nb-3Al	ST,WQ	β	82	
b	1998	6	Ti-15Mo-2.8Nb-3Al	ST,Ag	$\alpha+\beta$	100	
52	1998	6	Ti-15Mo-5Zr-3Al	ST,WQ	β	75	
b	1998	6	Ti-15Mo-5Zr-3Al	ST,Ag	$\alpha+\beta$	88- 113	
53	1998	21	Ti-16Nb-13Ta-4Mo	ST,WQ	β	46	
b	1998	21	Ti-16Nb-13Ta-4Mo	ST,Ag	β	98	
54	1998	21	Ti-29Nb-13Ta-4.6Zr	ST,CW	β	50	
b	1998	21	Ti-29Nb-13Ta-4.6Zr	ST,Ag	β	80	
c	2003	7	Ti-29Nb-13Ta-4.6Zr	ST,WQ	β	63	SE
d	2003	7	Ti-29Nb-13Ta-4.6Zr	ST,WQ+Ag	β	97	
e	2003	7	Ti-29Nb-13Ta-4.6Zr	ST,WQ+CW	β	62	SE
55	1998	52	Ti-30Ta	Sr	β	80	SME
b	1998	52	Ti-30Ta	ST,WQ	β	63	SME
56	1998	48	Ti-55.1Ni	ST,An	$\beta+\alpha''$	68	SME
57	1998	21	Ti-29Nb-13Ta	Ag	β	105	
58	1998	21	Ti-29Nb-13Ta-2Sn	ST,Ag	β	48	
59	1998	21	Ti-29Nb-13Ta-4.6Sn	ST,Ag	β	76	
60	1998	21	Ti-29Nb-13Ta-6Sn	ST,Ag	β	65	
61	1998	6	Ti-11.5Mo-6Zr-2Fe	ST	β	74-85	
62	1999	53	Ti-4Mo	Casted	$\alpha+\beta$		

63	1999	53	Ti-6Mo	Casted	β	64	
64	1999	53	Ti-7.5Mo	Casted	β	55	
65	1999	53	Ti-9Mo	Casted	$\beta+\alpha''$	75	
66	1999	53	Ti-10Mo	Casted	β	95	
67	1999	12	Ti-15Sn-4Nb-2Ta-0.2Pd-0.2O	ST,Ag	$\alpha+\beta$	100	
68	2000	54	Ti-24Nb-22Ta-4.5Zr	ST,WQ	$\beta+\alpha''+\omega$	55	
69	2000	54	Ti-22Nb-22Ta-4Zr	ST,WQ	$\beta+\alpha''+\omega$	65	
70	2000	54	Ti-29Nb-12.5Ta-7Zr	ST,WQ	$\beta+\omega$	50	
71	2000	54	Ti-35.5Nb-5Ta-7Zr	ST,WQ	$\beta+\omega$	56	
72	2000	54	Ti-35.1Nb-5.7Ta-7.2Zr	ST,WQ	$\beta+\omega$	48	
73	2001	55	Ti-16.6Nb-8.6Sn	ST,WQ,Ag	β		
74	2001	55	Ti-16.6Nb-10.6Sn	ST,WQ,Ag	β		SME
75	2001	55	Ti-16.6Nb-12.6Sn	ST,WQ,Ag	β		66
76	2001	55	Ti-20Nb-6.4Sn	ST,WQ,Ag	β		-20
77	2001	55	Ti-20Nb-8.6Sn	ST,WQ,Ag	β		66
78	2001	55	Ti-20Nb-10.6Sn	ST,WQ	β		SE
79	2001	55	Ti-22.8Nb-8.3Sn	ST,WQ,Ag	β		SME
80	2001	55	Ti-23.5Nb-8.3Sn	ST,WQ	β		SME
81	2001	55	Ti-24Nb-8.3Sn	ST,WQ	β		SME
82	2001	55	Ti-25Nb-8.2Sn	ST,WQ	β		SME
83	2001	19	Ti-15Zr-4Nb-4Ta-0.2Pd	ST,An	$\alpha+\beta+\alpha'$	100	
b	2001	19	Ti-15Zr-4Nb-4Ta-0.2Pd	ST, Ag	$\beta+\alpha'$	97	
84	2001	17	Ti-47.75Ni-5.78Cu-5.24Mo	Hr, Cd, ST	β		-8
85	2001	17	Ti-46.74Ni-5.68Cu-5.58Mo	Hr, Cd, ST	β		-18
86	2001	17	Ti-44.35Ni-5.45Cu-16.47Mo	Hr, Cd, ST	β		-103
87	2001	17	Ti-49.34Ni-5.93Cu	Hr, Cd, ST	β		SME
88	2002	56	Ti-24Nb-1.5Al-1Hf	ST,WQ	β	35	20
89	2003	7	Ti-6.42Al-4.19V ELI	ST, WQ	$\alpha+\beta$	118	
90	2003	7	Ti-13Nb-13Zr	ST,WQ	β	64	
b	2003	7	Ti-13Nb-13Zr	ST,WQ,Ag	β	81	
c	2003	7	Ti-13Nb-13Zr	ST,AC	β	83	
d	2003	7	Ti-13Nb-13Zr	ST,WQ,CW	β	44	
91	2003	57	Ti-25Nb-10Sn	ST,WQ	β		SE
92	2003	58	Ti-13Mo-5.3Ga	ST,WQ	β		SME
93	2003	58	Ti-11.2Mo-4.1Ga	ST,WQ	β		SME
94	2002	59	Ti-40Ta	ST,WQ	$\beta+\alpha''$		350
95	2002	59	Ti-50Ta	ST,WQ	$\beta+\alpha''$		400
96	2004	60	Ti-27.87Nb-11.87Sn	ST,WQ	β	40	
97	2004	60	Ti-32.52Nb-4.75Sn	ST,WQ, CW	β	43	
98	2004	61	Ti-13Mo-7Zr-3FeTMZF	ST,Ag, AC	β	89	
99	2004	62	Ti-14Nb	ST,An	$\alpha+\beta$	95	
100	2004	62	Ti-16 Nb	ST,An	$\alpha+\beta$	88	
101	2004	62	Ti-18 Nb	ST,An	$\alpha+\beta$	84	
102	2004	62	Ti-20 Nb	ST,An	$\alpha+\beta$	84	

103	2004	62	Ti-22 Nb	ST,An	$\alpha+\beta$	78	
104	2004	62	Ti-30 Nb	ST, WQ	$\alpha+\beta+\omega$	70	
105	2004	63	Ti-34Nb-9Zr-8Ta	ST,Ag	β	89	
106	2004	20	Ti-35Nb-5Ta-7Zr	ST,WQ	β		SE
107	2004	63	Ti-30Nb-13Ta-5Zr (TNZT30)	ST,AC	β		SE
108	2004	62	Ti-36Nb	ST,WQ	$\beta+\omega$	77	
109	2004	62	Ti-40Nb	ST,WQ	$\beta+\omega$	55	
110	2004	62	Ti- 38Nb	ST,WQ	$\beta+\omega$	66	SME
111	2004	62	Ti-28Nb	ST,WQ	$\alpha+\beta$	82	
112	2004	62	Ti-32Nb	ST,WQ	$\alpha+\beta+\omega$	85	
113	2004	20	Ti-40Nb-1Hf	ST, An, FC	$\beta+\omega$	65	
114	2004	20	Ti-40Nb-3Hf	ST, An, FC	$\beta+\omega$	62	
115	2004	20	Ti-40Nb-5Hf	ST, An, FC	$\beta+\omega$	67	
116	2004	20	Ti-40Nb-7Hf	ST, An, FC	$\beta+\omega$	63	
117	2004	16	Ti-38.41Nb-1.4Al	ST,WQ,ST,WQ	$\beta+\omega$		-72
118	2004	64	Ti-9,54Mo	ST,HW,CW,ST,WQ	$\beta+\alpha''$		SME
119	2004	64	Ti-11,34Mo	ST,HW,CW,ST,WQ	$\beta+\alpha''$		SME
120	2004	64	Ti-9,15Mo-6,80Sn	ST,HW,CW,ST,WQ	β		SME
121	2004	64	Ti-9Mo-10.12Ag	ST,HW,CW,ST,WQ	$\beta+\alpha''$		SME
122	2005	65	Ti-36Nb-3.1Zr	CW, ST,WQ	β		37
123	2005	65	Ti-33.4Nb-12Zr	CW, ST,WQ	β		-60
124	2006	66	Ti-51.2Ni-9.5Ta	ST,An,WQ	β		58
125	2006	66	Ti-49Ni-15.1Ta	ST,An,WQ	β		44
126	2006	66	Ti-46.2Ni-14.5Ta	ST,An,WQ	β		55
127	2006	67	Ti-30Nb-3Pd	ST,WQ, An,WQ	$\beta+\omega+\alpha''$		SME
128	2006		Ti-24.73Nb-24.70Ta	ST,WQ	β	75	
129	2006		Ti-21.40Nb-20.13Ta	ST,WQ	$\beta+\alpha''$	78	
130	2006		Ti-13.7Nb-1.4Ta	ST,WQ	$\beta+\alpha''$	72	125
131	2006		Ti-48.50Nb-1Zr	ST,WQ	β	79	
132	2006		Ti-41.20Nb-6.10Zr	ST,WQ	β	67	
133	2006		Ti-29.50Nb-7.13Zr	ST,WQ	$\beta+\alpha''$	78	
134	2006		Ti-19.1Nb-8.8Zr	ST,WQ	$\beta+\alpha''$	74	45
135	2006	27	Ti-25Nb	ST,WQ	β	60-70	
136	2006	27	Ti-30Nb-1Fe	ST,WQ	β	60-70	
137	2006	27	Ti-50Ta-20Zr	ST,WQ	β	60-70	
138	2006	27	Ti-34.78Zr-11.81Nb-23Ta	ST,WQ	β	44	
139	2007	68	Ti-30,30Mo-3,34Cu	ST,WQ,CW,ST,WQ	$\beta+\alpha''$		SME
140	2007	68	Ti-30,22Mo-4,45Cu	ST,WQ,CW,ST,WQ	β		SE
141	2007	68	Ti-30,13Mo-5,54Cu	ST,WQ,CW,ST,WQ	β		SE
142	2007	68	Ti-30,05Mo-6,64Cu	ST,WQ,CW,ST,WQ	β		SE
143	2007	69	Ti-26,35Nb-9,76Pt	ST,CW,An,WQ	α''		SME
144	2007	69	Ti-27,03Nb-12,61Pt	ST,CW,An,WQ	$\beta+\alpha''$		SE
145	2007	69	Ti-27,67Nb-15,29Pt	ST,CW,An,WQ	$\beta+\alpha''$		SE
146	2007	69	Ti-28,28Nb-17,81Pt	ST,CW,An,WQ	$\beta+\alpha''$		SE

For Peer Review Only

Table 3. Chemical composition (wt.%), β -transus temperature ($^{\circ}\text{C}$) [48], Mo. equivalence (%) [48], microstructure, M_s temperature ($^{\circ}\text{C}$) or thermoelastic phase transformation detected by cyclic nanoindentation (TPT), and elastic modulus values (GPa) for each alloy fabricated in our laboratory.

Chemical composition	Nr. alloy	β transus temperature	Mo.eq.	Microstructure	M_s temperature	E, 5%error
Ti-24.73Nb-24.70Ta	128	649	12,4	β	TPT	75
Ti-21.40Nb-20.13Ta	129	683	10,4	β +some α''	TPT	78
Ti-13.7Nb-1.4Ta	130	780	4,1	mainly α''	125 TPT	72
Ti-48.50Nb-1Zr	131	532	13,6	β	-	79
Ti-41.20Nb-6.10Zr	132	584	11,6	β	-	67
Ti-29.50Nb-7.13Zr	133	669	8,3	β +some α''	-	78
Ti-19.1Nb-8.10Zr	134	713	6,6	mainly α''	45 TPT	74