Molar volumes of bcc, hcp, and orthorhombic Ti-base solid solutions at room temperature

Jia-Yi Yan

Department of Materials Science and Engineering, KTH Royal Institute of Technology,

Brinellvägen 23, SE-100 44 Stockholm, Sweden

jiayian@kth.se (corresponding author)

G.B. Olson

Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive,

Evanston, Illinois 60208-3108, USA

g-olson@northwestern.edu

Abstract

The room-temperature molar volumes of bcc (β), hcp (equilibrium α or martensitic α'), and orthorhombic (martensitic α'') phases are modeled for a number of Ti-base solid solutions in the CALPHAD framework. The martensitic molar volume is continuous at the α'/α'' transition composition. Hcp and orthorhombic structures are modeled separately, and the predicted martensitic structure is taken as the denser one.

Keywords: Molar volume; Titanium alloys; Martensite

1. Introduction

Computational materials design, as a well-recognized approach to accelerated materials development, is to be supported by fundamental databases understood as the Materials Genome.[1] The CALPHAD database system, originated from phase-equilibria descriptions, has proven indispensable in designing materials microstructure[2, 3]. In response to an increasing demand of materials design in a broader context, CALPHAD also extends to other phase-level attributes such as molar volumes[4-6], atomic mobilities[7], and elastic moduli[5]. A specific example is designing transformation-toughened titanium alloys[8-10]: The toughening effect is sensitive to the martensitic transformational dilatation, as revealed by the mechanistic models of transformation toughening developed from steel research [11-13]. Therefore an accurate molar-volume database of Ti-base solid solutions is in need.

Martensite in Ti alloys has a crystal structure of either hexagonal close-packed (hcp, α') or orthorhombic (α''), transformed from the parent body-centered cubic (bcc, β) phase. The lattice correspondences of the three phases are shown in Figure 1. The net deformation of a semicoherent martensitic transformation is described by an invariant-plane strain, composed of a

shear on the invariant plane and a dilatation normal to it. For the purpose of modeling martensitic dilatation, we have built up a room-temperature molar volume database of bcc, hcp and orthorhombic phases. This database can also be used to calculate the room-temperature molar volume of equilibrium α phase, which has the same hcp structure with α' martensite. Extension of the current database to include temperature and pressure is an important next step, but it is currently limited by data availability. The room-temperature database is sufficient for the particular purpose of designing transformation-toughened titanium alloys serving at room temperature.

In some Ti systems there exists a transition of martensitic structure from hcp to orthorhombic with increasing solute content. The orthorhombic martensite is not a distinct new phase but a distorted hcp. This orthorhombic distortion is of the same nature with the tetragonal distortion of substitutional ferrous martensite from bcc to bct (body-centered tetragonal). In both cases the distortion relaxes the full bcc/hcp or fcc/bcc Bain strain and gives an intermediate structure. Cahn and Rosenberg explained such distortion by an anisotropy of pair correlation brought about by short-range ordering in the parent phase[14, 15]. Lattice parameters of Ti-Mo, Ti-Nb and Ti-Ta martensites do not show a discontinuity greater than experimental scatter at the α'/α'' transition composition (Figure 2). Therefore the molar volume is assumed continuous at the α'/α'' transition point.

In this work, we model the room-temperature molar volumes of bcc, hcp and orthorhombic phases in the CALPHAD framework. We take the orthorhombic phase as a distinct phase instead of distorted-hcp, due to a lack of information on the α'/α'' transitional composition and the amplitude of distortions for multi-component alloys. Literature results are used as much as possible. For the α'' martensite in ternary Ti-V-Al and quaternary Ti-V-Al-Fe system, we have

made a number of experimental alloys and measured their martensitic lattice parameters using X-ray diffraction (XRD).

2. Lattice parameters of α'' martensite of Ti-V-Al and Ti-V-Al-Fe alloys

A number of Ti-V-Al and Ti-V-Al-Fe alloys (named “Bx-y-z”) were arc melted as buttons of 3-5 grams. The weight change before and after arc melting was less than 0.005%, therefore the nominal compositions are used. The oxygen and nitrogen contents of the buttons were about 580 wppm O and 53 wppm N, as measured by LECO analyzer. After solutionizing and quenching in iced brine, all the buttons showed a martensitic microstructure. The buttons were then cold-rolled and ground to obtain a broad flat surface. A subsequent solutionization-and-quenching treatment was carried out to obtain quenched martensite from recrystallized β grains. The sample surface was slightly polished by an aqueous solution of 20% HNO_3 and 1% HF to remove the thin passivated layer as a result of water contact during quenching. Mechanical grinding and polishing were avoided between heat treatment and lattice parameter measurement, because of the sensitivity of the quality of diffraction patterns of Ti alloys to surface deformation.

The X-ray scans were conducted on a Scintag XDS2000 diffractometer using a Cu target. θ - 2θ step scans were carried out with a 2θ step size smaller than 0.1° and a stepwise dwelling time of 4 seconds. Diffraction peak profiles were fit to pseudo-Voigt functions for precise peak locations. Cohen’s least-square fitting method[51] was used for precise lattice parameter determination for orthorhombic structure and diffractometer setup, which gave the values of a , b and c parameters of the α'' phase and their standard deviations. The peaks at $2\theta < 70^\circ$ were adopted, because the peaks at higher angles were of lower qualities for precise lattice parameter

determination. Some peaks of retained bcc phase were also identified. However, high-quality bcc peaks were too few for reliable determination of the bcc lattice parameter.

Figure 3 shows the diffraction pattern of the B14-5.5-0 alloy. The patterns of other alloys are very similar except with slight shifts of peak positions. The lattice parameters of Bx-y-z alloys are listed in Table 1, together with relevant literature data. These lattice parameters are used for molar volume calculation and subsequent fitting.

3. Modeling

For the molar volume V_m of phase ϕ , we use a linear mixture of pure elements plus a regular-solution model for the excess volume:

$$V_m^\phi = \sum_i x_i V_{m,i}^\phi + \sum_{i < j} x_i x_j \Omega_{(i,j)}^\phi$$

where x_i denotes the molar fraction of element i , and Ω is the molar volume interaction parameter.

3.1 Bcc phase

Lattice parameters of Ti-Fe/Mo/Nb-Ta/V binary systems are available from literature. Because bcc pure Ti is not stable at room temperature, its lattice parameter $a_\beta(\text{Ti})$ is determined by extrapolating multiple binary Ti systems as 3.282Å [56], corresponding to a molar volume of $10.64 \times 10^{-6} \text{m}^3/\text{mol}$. The bcc molar volumes of Fe, Mo, Ta, and V are taken from the assessment by Lu *et al.* [57], and that of Nb from Grad *et al.* [58]. Using the molar volumes of pure elements, the excess molar volumes are calculated and fit to the regular solution model (Figure 4).

Because the bcc phase is not stable in the Ti-Al/Sn/Zr binary systems, the effects of Al, Sn and Zr on bcc molar volumes are taken from ternary alloys Ti-Nb/V-Al/Sn/Zr. The bcc molar volumes of pure Al and Sn are taken from the density-functional-theory calculations by Wang *et*

al. [86]. For Zr, we adopt the assessment by Lu *et al.* [57] based on an extrapolation of the bcc Zr-Nb system. The interaction parameters are determined by fitting to experimental data from the literature. (Figure 5)

3.2 Hcp phase

Lattice parameters of pure hcp Ti at room temperature have been measured by a number of researchers. We use the values from Dechamps *et al.* [89] ($a=2.9512\text{\AA}$, $c=4.6874\text{\AA}$, $V_m=10.635\times 10^{-6}\text{m}^3/\text{mol}$) as determined by extrapolating hcp Ti-O alloys to pure Ti. The hcp molar volumes of other pure elements are taken from experimental assessments[57], and from density-functional theory (DFT) calculations[86] if no experimental assessment is available. Excess volume terms are obtained by fitting to experimental data of equilibrium α phase (Ti-Al/Zr) or α' martensite (Ti-Fe/Mo/Nb/Ta/V) (Figure 6).

3.3 Orthorhombic phase

Since orthorhombic α'' martensite is regarded as a distinct phase in our CALPHAD approach, we first have to determine the molar volumes of the hypothetical orthorhombic phases of pure elements. We start from the three binary systems Ti-Mo, Ti-Nb, and Ti-Ta, where the lattice parameters of α'' martensite have been abundantly reported. A direct fit of molar volume to experimental data is not satisfactory due to large scatter and uncertainty. Instead, we use piecewise linear equations to fit the lattice parameters of the α' and α'' phases (Figure 2), calculate the molar volumes using the formulated lattice parameters, and then find the regular-solution-type equations that best describe the calculated molar volumes. We also assume a continuity of molar volumes at the α'/α'' transitional composition. By this means we find that a common intercept of $10.76\times 10^{-6}\text{m}^3/\text{mol}$ for the orthorhombic pure Ti is appropriate. The molar

volumes of orthorhombic Mo, Nb, and Ta, with their interaction parameters with Ti, are determined by fitting. (Figure 7)

Using this method, in the Ti-Mo, Ti-Nb and Ti-Ta systems the α'/α'' transition is determined by an intersection of their molar volumes, and the phase with a smaller molar volume is determined as the actual martensitic structure.

The molar volumes of the hypothetical α'' phase of other pure elements are determined by linear fitting (zero excess volume). Regarding the Al-containing α'' phase, Figure 2(a) shows that an addition of 3wt% Al (~5.5at% Al) does not change the lattice parameters of the Ti-Mo α'' phase, based on the measurements by Sasano et al.[20]. In Figure 2(b), data from Inamura et al.[38] show that 3at% Al does not change the lattice parameters of the Ti-Nb α'' phase either. Based on these observations, $V_m^{\text{ort}}(\text{Al})$ is set equal to $V_m^{\text{ort}}(\text{Ti})$. The α'' molar volumes of V and Fe, and necessary excess volumes are determined by a multiple-linear regression of the experimental data from Table 1 and summarized in Figure 8. $V_m^{\text{ort}}(\text{Sn})$ is determined from multiple Ti-Ta-Sn alloys [88]. $V_m^{\text{ort}}(\text{Zr})$ is estimated assuming $V_m^{\text{ort}}(\text{Zr}) - V_m^{\text{hcp}}(\text{Zr}) = V_m^{\text{ort}}(\text{Ti}) - V_m^{\text{hcp}}(\text{Ti})$.

The assessed parameters for molar volume modeling are listed in Table 2.

5. Discussion

The dilatation of the β -to- α'/α'' martensitic transformation can be calculated using the current molar-volume assessment and the smaller-volume criterion, for the transformation induced at room temperature:

$$\Delta V / V = (V_m^{\text{mart}} - V_m^{\text{bcc}}) / V_m^{\text{bcc}}, \quad V_m^{\text{mart}} = \min \{V_m^{\text{hcp}}, V_m^{\text{ort}}\}$$

Figure 9 shows the room-temperature transformation dilatations of binary Ti-X systems. The curves are truncated at the critical composition beyond which the β phase is fully retained after quenching. For these systems, adding alloying elements promotes the bcc-hcp transformation dilatation, yet reduces the bcc-ort dilatation once it crosses the α'/α'' transitional composition. This is consistent with the notion that the orthorhombic martensite corresponds to an incomplete Bain strain and with an intermediate structure between bcc and hcp. In the context of transformation-toughened Ti alloy design, it is desirable to tailor the martensitic structure close to the α'/α'' transitional point, in order to obtain a relatively large transformation dilatation.

The accuracy of the current assessment is primarily limited by experimental uncertainties. From Figures 3-7 one may expect a relative uncertainty of about 1% for V_m^{hcp} and V_m^{ort} , and perhaps slightly smaller for V_m^{bcc} . Although this is quite satisfactory for molar volume *per se*, the uncertainty is often comparable to the magnitude of transformation dilatation. Nevertheless, the current assessment is capable of suggesting directions for larger transformation dilatation in titanium alloy design. We also notice an artifact in the binary Ti-Fe system: While experimentally the martensite is hcp up to 3at%Fe (Figure 6b), an α'/α'' transition at 1.6at%Fe is predicted by the smaller-volume criterion with the parameters from Table 2. Despite the inconsistency in the binary Ti-Fe system, the current model describes the Ti-V-Al-Fe system reasonably well, which is probably of more technical interest.

6. Conclusions

The room-temperature molar volumes of bcc (β), hcp (α or α') and orthorhombic (α'') phases in Ti-base alloys are modeled in the CALPHAD framework. For the Ti-Mo, Ti-Nb and Ti-Ta systems, the molar volume is taken to be continuous at the α'/α'' transition point. We

model α' and α'' martensites as two distinct phases, and assume the actual martensitic structure is the one with a denser structure.

Acknowledgments

This work is sponsored by the US Office of Naval Research through the Cyberalloys 2020 Project (No. N00014-10-1-0504), coordinated by Dr. William Mullins. QuesTek Innovations LLC is thanked for the arc-melting facility. Sergio Williams contributed to part of the lattice parameter measurements. This work made use of the J.B. Cohen X-Ray Diffraction Facility supported by the MRSEC program of the National Science Foundation (DMR-1121262) at the Materials Research Center of Northwestern University.

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Figure captions:

Figure 1. Equivalent representation of bcc (red), orthorhombic (blue), and hcp (gray) structures using an orthorhombic cell.

Figure 2. Room-temperature lattice parameters of α' and α'' martensites in Ti-Mo/Nb/Ta systems. Solid lines are piecewise linear fitting.

Figure 3. X-ray diffraction pattern of as-quenched B14-5.5-0 alloy with indices of α'' orthorhombic martensite (without subscript) and of retained β bcc phase (with subscript “b”).

Figure 4. Bcc molar volumes of Ti-Fe/Mo/Nb/V/Ta systems.

Figure 5. Bcc molar volumes of Ti-X-Al/Sn/Zr systems.

Figure 6. Hcp molar volumes of Ti-Al/Fe/Sn/V/Zr systems.

Figure 7. Molar volume of martensite in the Ti-Mo/Nb/Ta systems. Dashed curve: molar volume calculated by the piecewise linear fitting to the lattice parameters from Figure 2. Solid curve: regular-solution fitting. For the Ti-Nb system the dashed and solid curves overlap.

Figure 8. Measured versus calculated α'' molar volumes of the Ti-V-Al-Fe alloys listed in Table 1.

Figure 9. Calculated room-temperature martensitic dilatation of binary Ti alloys

Tables:

Table 1. Lattice parameters of Ti-V-Al-Fe α'' martensite

Data source	at% V	at% Al	at% Fe	a/Å	b/Å	c/Å	$\Delta a/\text{Å}$	$\Delta b/\text{Å}$	$\Delta c/\text{Å}$
B12-3-0	12.00	3.03	0	2.985	4.969	4.636	0.004	0.008	0.010
Yang <i>et al.</i> [52]	13	3	0	3.11	4.74	4.65	0.01	0.02	0.02
B13.5-3-0	13.50	3.03	0	3.009	4.932	4.629	0.003	0.005	0.008
Yang <i>et al.</i> [52]	13	5	0	3.21	4.66	4.61	0.02	0.03	0.03
B12-5.5-0	11.97	5.53	0	2.989	4.918	4.622	0.005	0.008	0.012
B13.5-5.5-0	13.49	5.55	0	2.988	4.914	4.621	0.004	0.007	0.010
B14-5.5-0	14.02	5.53	0	3.000	4.918	4.622	0.004	0.007	0.010
B14.3-5.5-0	14.34	5.55	0	2.995	4.921	4.628	0.002	0.003	0.004
B14.5-5.5-0	14.47	5.52	0	3.004	4.896	4.604	0.007	0.009	0.016
B13-7-0	13.03	7.03	0	2.982	4.924	4.625	0.003	0.004	0.006
B13.4-7-0	13.38	6.95	0	2.979	4.922	4.638	0.002	0.004	0.006
B13.5-7-0	13.51	6.99	0	2.972	4.963	4.637	0.003	0.005	0.006
Pak <i>et al.</i> [53]	14.17	6.95	0	2.990	4.900	4.570	--	--	--
B12-10-0	11.75	10.24	0	2.972	4.930	4.632	0.002	0.004	0.005
Takemoto <i>et al.</i> [54]	0	5.23	3.37	2.965	5.061	4.620	--	--	--
	0	6.92	3.34	2.983	5.039	4.693	--	--	--
	0	8.59	3.31	2.976	4.983	4.662	--	--	--
	0	11.85	3.27	2.995	4.913	4.659	--	--	--
B10-5.5-1	10.10	5.52	0.99	2.977	4.955	4.639	0.003	0.005	0.008

B12-5.5-0.5	12.00	5.50	0.50	2.987	4.928	4.626	0.003	0.004	0.007
Duerig <i>et al.</i> [55]	8.60	5.59	1.52	3.01	4.91	4.63	--	--	--
B7-7-2	7.10	7.00	2.00	2.984	4.929	4.632	0.003	0.005	0.006

Table 2. The assessed parameters of molar volumes of β , α' , and α'' phases, in $10^{-6}\text{m}^3/\text{mol}$

	V_m^{bcc}	$\Omega_{(\text{X,Ti})}^{\text{bcc}}$	V_m^{hcp}	$\Omega_{(\text{X,Ti})}^{\text{hcp}}$	V_m^{ort}	$\Omega_{(\text{X,Ti})}^{\text{ort}}$
Ti	10.644	-----	10.635	-----	10.76	-----
Fe	7.008	-3.13	6.115	1.29	0.00	0.00
Mo	9.346	-1.07	9.766	0.88	5.29	0.00
Nb	10.821	-0.12	11.343	1.09	9.03	1.57
Ta	10.787	-0.66	11.297	1.04	9.95	0.60
V	8.248	0.00	9.103	0.00	8.61	0.00
Al	10.279	-1.30	10.110	-1.50	10.76	0.00
Sn	17.049	-4.11	16.747	-4.67	15.96	0.00
Zr	13.812	0.00	13.952	0.00	14.07	0.00
Cross terms	$\Omega_{(\text{V,Zr})}^{\text{bcc}} = 24.09$				$\Omega_{(\text{Al,V})}^{\text{ort}} = -26.20$	

Figure1

Structure	Lattice parameters	Shuffle	Molar volume (N_A =Avogadro's number)
bcc (β)	$b/a = c/a = \sqrt{2}$	$\delta/b = 0$	$V_m^{\text{bcc}} = N_A a^3/2$
orthorhombic(α'')	$\sqrt{2} < b/a < \sqrt{3}$	$0 < \delta/b < 1/6$	$V_m^{\text{ort}} = N_A abc/4$
hcp(α')	$b/a = \sqrt{3}$	$\delta/b = 1/6$	$V_m^{\text{hcp}} = N_A a^2 c(\sqrt{3}/4)$

Figure2

(b) Ti-Nb martensite

(a) Ti-Mo martensite

(c) Ti-Ta martensite

Figure3

Figure4

Figure5

Figure6

Figure 7

Figure8

Figure9