

## Short communication

# Lattice expansion of Ti–6Al–4V by nitrogen and oxygen absorption

R. Montanari<sup>a,\*</sup>, G. Costanza<sup>a</sup>, M.E. Tata<sup>a</sup>, C. Testani<sup>b</sup>

<sup>a</sup>Dipartimento di Ingegneria Meccanica, Università di Roma-Tor Vergata, Via del Politecnico 1, 00133 Roma, Italy

<sup>b</sup>Centro Sviluppo Materiali, Castel Romano, Via di Castel Romano 100, 00128 Roma, Italy

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### ABSTRACT

The effects of nitrogen and oxygen absorption on lattice expansion of Ti–6Al–4V have been investigated by high-temperature X-ray diffractometry. Experiments have been performed on stress-free powder for its high surface–volume ratio and to avoid possible effects on diffraction patterns due to texture change and recovery of defective structures induced by the measurement cycle at temperature. Cell parameters  $a$  and  $c$ , measured at increasing temperatures up to 600 °C, show linear trends with different slopes. As temperature increases, the cell volume expands and the  $c/a$  ratio changes. This is due to both lattice thermal expansion and absorption of oxygen and nitrogen. Part of the gas remains entrapped in the metal after cooling to room temperature causing a residual lattice distortion. Results have been compared with literature data obtained in analogous tests performed on bulk Ti–6Al–4V alloy both in vacuum and in inert gas atmosphere.

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## 1. Introduction

Mechanical and physical properties of titanium and titanium alloys strongly depend on interstitial elements in solid solution, in particular nitrogen and oxygen [1–7]. Their solubility in both the  $\alpha$  and  $\beta$  phases of titanium is high and increases with temperature. This plays an important role in different industrial processes such as hot-working, stress relief heat treatments and sintering.

In spite of the widespread use of titanium and titanium alloys, in particular for high-temperature applications, only recently have results of investigations by high-temperature X-ray diffraction (HT-XRD) been published [8–10]. In the present work HT-XRD has been employed to examine Ti–6Al–4V powder heated up to 600 °C in argon of commercial purity. Experiments have been performed on stress-free powder, for its high surface–volume ratio, enhancing gas absorption. In

addition, the use of powder avoids effects on diffraction patterns due to texture change and recovery of defective structures induced by the measurement cycle at temperature.

## 2. Material and Experimental

The Ti–6Al–4V alloy examined had the following chemical composition: Al 5.85, V 4.2, Fe 0.15, Ti to balance (wt.%). Powder was prepared by atomization under inert gas; particles had a mean size of about 20  $\mu\text{m}$  (see Fig. 1). The XRD pattern collected at room temperature showed only the presence of the  $\alpha$  phase (Fig. 2).

Measurements at high temperature were performed by means of an Anton Paar HT-16 camera in argon. The gas composition ( $\text{O}_2$  1 ppm/mol,  $\text{N}_2$  2 ppm/mol,  $\text{H}_2\text{O}$  1 ppm/mol, total hydrocarbon gases 0.02 ppm/mol) is similar to that

\* Corresponding author. Tel.: +39 06 72597182; fax: +39 06 20213511.

E-mail address: roberto.montanari@uniroma2.it (R. Montanari).

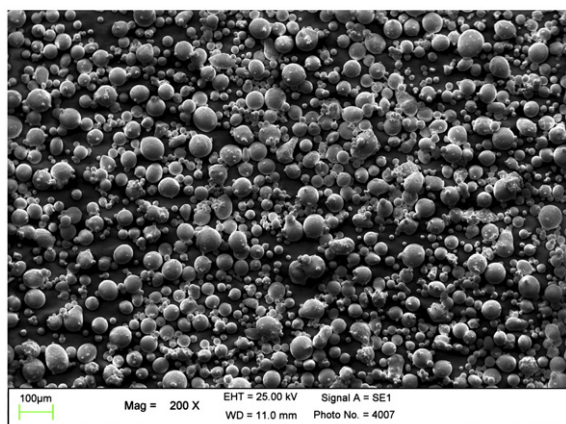


Fig. 1 – SEM micrograph of Ti-6Al-4V powder.

usually employed in industrial heat treatments (no analytical purity). Temperature was controlled by a thermocouple in direct contact with the samples.

The samples were tested in isothermal conditions at increasing temperatures up to 600 °C with steps of 100 °C. The procedure consisted of successive stages; in each stage the sample was rapidly heated ( $\sim 1$  °C s $^{-1}$ ) to the test temperature and kept there for 600 s to guarantee thermal stabilization before recording the XRD spectra. After the completion of measurements, the same operations were repeated for the successive temperatures, and so on.

In a first group of experiments, Mo-K $\alpha$  radiation ( $\lambda = 0.071$  nm) was employed to get a large number of reflections. At each temperature the whole spectrum was collected by step-scanning with steps of 0.05° and a counting time of 2 s per step. Precision peak profiles of the most intense reflections, {100}, {002}, {101}, {102}, {110} and {103}, were then recorded using 0.005° steps and counting times of 10 s per step. To get higher precision in determining the central peak positions, a second group of tests was performed with Co-K $\alpha$  radiation ( $\lambda = 0.179$  nm), using an iterative procedure. This consisted of successive measurement runs on progressively narrower

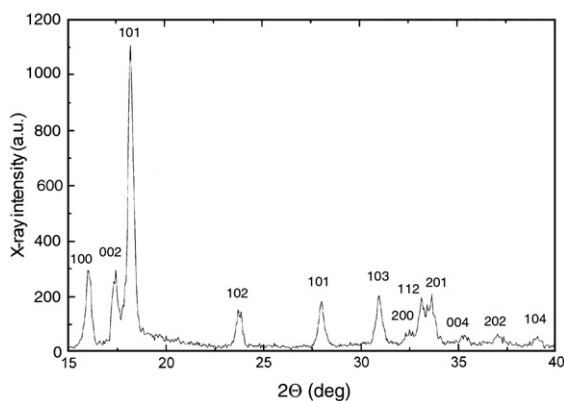


Fig. 2 – XRD pattern of Ti-6Al-4V powder in its original condition. The data are from room temperature measurements using Mo-K $\alpha$  radiation.

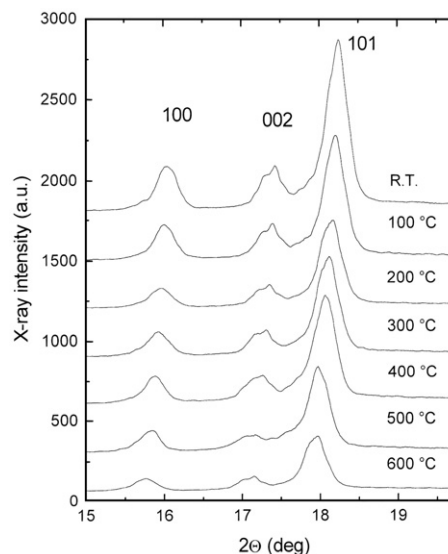


Fig. 3 – Precision peak profiles of {100}, {002} and {101} reflections at increasing temperatures up to 600 °C (Mo-K $\alpha$  radiation).

angular ranges around the peak using longer counting times (up to 100 s).

In some calibration tests Al $_2$ O $_3$  powder was used as an internal standard for  $2\theta$  correction. From interplanar spacings,  $d_{hkl}$ , of the six most intense reflections the cell parameters,  $a$  and  $c$ , were calculated with an accuracy of  $\pm 0.00002$  nm.

After each measurement cycle the samples were cooled to room temperature and retested to assess possible variations with respect to the original state.

Chemical analyses were performed before and after each measurement cycle to determine directly the amount of oxygen and nitrogen in the alloy; these results were compared with those from XRD. The specimens had been molten under inert gas (He) in a graphite crucible, thus the possibility of contamination was considered. Analysis for nitrogen was carried out by means of a thermo-conductivity cell, while for oxygen an infrared cell (CO $_2$ ) was used.

### 3. Results and Discussion

As the test temperature increased, the XRD peak intensities become progressively weaker and their central positions shift toward lower angles. For example, Fig. 3 displays the change of the first three reflections up to 600 °C. The interplanar spacings,  $d_{hkl}$ , of the six most intense reflections, determined from XRD peak positions measured using Co-K $\alpha$  radiation, are reported in Table 1. Cell parameters ( $a$ ,  $c$ ) were calculated from  $d_{hkl}$  values.

Fig. 4 shows  $a$  and  $c$  plots vs. temperature; experimental data were fitted by the following relationships:

$$a = a_0(1 + \alpha\Delta T) \quad (1)$$

$$c = c_0(1 + \beta\Delta T) \quad (2)$$

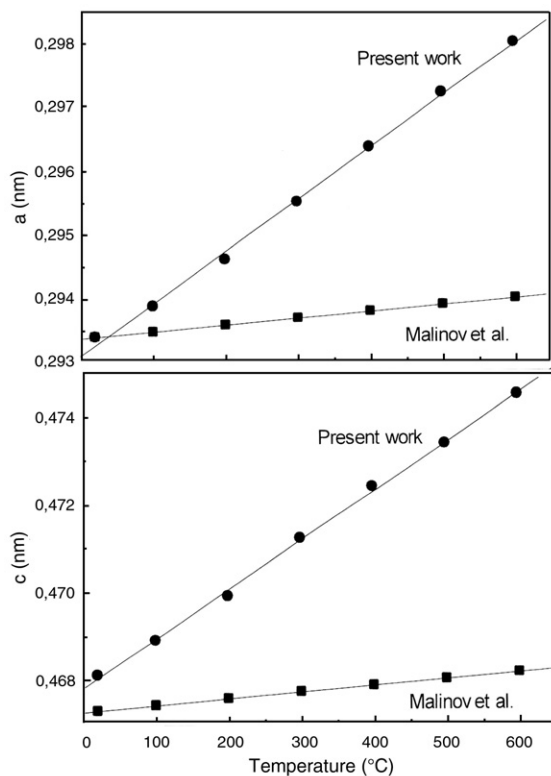
**Table 1**–Interplanar spacings  $d_{hkl}$  (nm) of Ti-6Al-4V powder at increasing temperatures up to 600 °C

hkl	25 °C	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
100	0.2540	0.2545	0.2548	0.2552	0.2555	0.2558	0.2563
002	0.2340	0.2345	0.2350	0.2356	0.2361	0.2366	0.2368
101	0.2229	0.2234	0.2237	0.2241	0.2245	0.2250	0.2252
102	0.1722	0.1723	0.1727	0.1730	0.1734	0.1735	0.1739
110	0.1464	0.1466	0.1468	0.1469	0.1472	0.1473	0.1476
103	0.1329	0.1330	0.1333	0.1335	0.1337	0.1341	0.1344

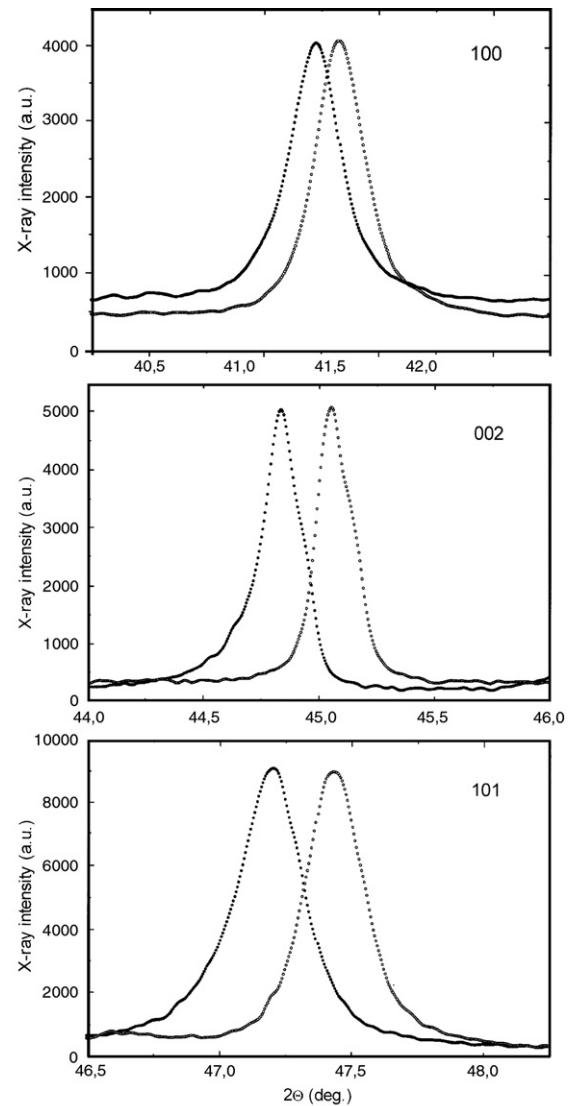
where  $a_0=0.29340$  nm and  $c_0=0.46810$  nm are the cell parameters at room temperature (25 °C),  $\alpha$  and  $\beta$  the expansion coefficients, and  $\Delta T$  the temperature increase. From the fitting,  $\alpha=2.32 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  and  $\beta=2.42 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  were obtained.

Both cell parameters linearly increase with temperature but not at the same rate; in fact,  $c$  grows more rapidly than  $a$ , thus the hcp unit cell expands, modifying its shape.

Results of analogous experiments performed on bulk Ti-6Al-4V alloy are reported in the literature [8–10]. The expansion coefficients determined from tests in vacuum (pressure of  $2.5 \times 10^{-3}$  mbar) [8] were  $\alpha=1.043 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  and  $\beta=1.448 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ , and those measured in an argon atmosphere [9] were  $\alpha=1.10 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  and  $\beta=1.24 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ ; these values do not exhibit remarkable differences. The  $\alpha$  and  $\beta$  values of the bulk alloy are always lower than those determined in the present experiments on powder. For comparison, the data of Malinov et al. [8] are contrasted with the present results in Fig. 4.



**Fig. 4**–Cell parameters ( $a$  and  $c$ ) for the Ti-6Al-4V powder as a function of temperature. The data of Malinov et al. [8] obtained by testing bulk Ti-6Al-4V alloy in vacuum (pressure of  $2.5 \times 10^{-3}$  mbar) are reported for comparison.



**Fig. 5**–{100}, {002} and {101} XRD reflections before (solid circles) and after (open circles) the at-temperature measurement cycle (Co-K $\alpha$  radiation). Peak intensities have been normalised to make the comparison easier. Observe the peak shifts to lower angles at room temperature.

The differences displayed by Fig. 4 can be ascribed to the atmosphere because argon of commercial purity contains residual amounts of oxygen and nitrogen, which are absorbed by the metal during annealing. The higher the temperature, the greater their concentration in the lattice. Therefore, the cell expansion at high temperature has two components: one is thermal, the other is due to gas absorption.

In our experiments the effect of gas absorption on lattice variations is significantly remarkable because of the large surface–volume ratio for our powder, whereas for bulk material smaller differences between tests performed in argon and vacuum are reported [8–10].

To assess whether part of the gas remains entrapped in the lattice after cooling to room temperature, the samples were examined after each test run. Fig. 5 displays the {100}, {002} and {101} reflections before and after the test run; after cooling to

room temperature the XRD spectra show peak shifts towards lower angles.

After cooling, the cell parameters ( $a=0.29402$  nm,  $c=0.47010$  nm) are greater than those of the original material; in an analogous manner the cell volume increases from  $0.1047$  to  $0.1056$  nm<sup>3</sup> and the  $c/a$  ratio from  $1.5954$  to  $1.5989$ .

When metal is cooled to room temperature, the thermal component of the lattice expansion disappears while the component due to gas absorption disappears only if the gas is completely released. The residual expansion observed after cooling indicates that part of the gas absorbed during the measurement cycle at high temperature remains entrapped in the lattice.

Oxygen and nitrogen occupy the octahedral interstices in hcp metals. The strain induced by the interstitials in the crystal lattice along the Z-axis, perpendicular to the basal plane, is greater than that along the X- and Y-axes lying in the basal plane. Lattice expansion due to foreign atoms in interstitial positions has been theoretically explained on the basis of the concept of elastic dipoles [11,12].

The length change of  $a$  and  $c$  in titanium as a function of the amount,  $\eta$ , of interstitial atoms in the lattice,  $da/d\eta$  and  $dc/d\eta$ , respectively, is  $9.0 \times 10^{-5}$  and  $4.0 \times 10^{-4}$  for oxygen,  $2.0 \times 10^{-4}$  and  $6.7 \times 10^{-4}$  for nitrogen [2], expressed in nm (at.%)<sup>-1</sup>.

Both  $da$  and  $dc$  are the sum of two terms, namely the contributions of oxygen and nitrogen. Owing to absorption of both oxygen and nitrogen, the change of  $a$  and  $c$  can be written as:

$$a = a_0 + da = a_0 + \left[ \left( \frac{da}{d\eta} \right)_O + \left( \frac{da}{d\eta} \right)_N \right] \quad (3)$$

$$c = c_0 + dc = c_0 + \left[ \left( \frac{dc}{d\eta} \right)_O + \left( \frac{dc}{d\eta} \right)_N \right] \quad (4)$$

After the measurement cycle at high temperature the chemical analyses indicated an increase  $d\eta_O=0.632$  at.% of oxygen and  $d\eta_N=0.453$  at.% of nitrogen. Substituting these data and the values of  $da/d\eta$  and  $dc/d\eta$  reported in [2] in Eqs. (3) and (4),  $a=0.29358$  nm and  $c=0.46878$  nm are obtained. Within experimental error these values are in agreement with those determined by the present XRD measurements.

#### 4. Conclusions

HT-XRD examinations of Ti-6Al-4V powder have been performed at increasing temperatures up to 600 °C in an argon atmosphere. The results show that  $a$  and  $c$  increase linearly as temperature increases. The  $a$  and  $c$  lengths change at different rates; thus, the unit cell expands, modifying its shape.

The values of the expansion coefficients determined in the present experiments are greater than those reported in the

literature for bulk Ti-6Al-4V alloy, tested in vacuum or in an argon atmosphere.

At high temperature, the volume and shape variations of the unit cell are due to both thermal expansion and absorption of nitrogen and oxygen residually present in the argon atmosphere. The absorption of gas strongly depends on the surface-volume ratio; thus, its contribution is greater for powder than for bulk material.

XRD and chemical analyses showed that part of the gas absorbed at high temperature remains entrapped in the metal after cooling to room temperature, causing lattice distortion.

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