J Mater Sci (2008) 43:5977–5981
DOI 10.1007/s10853-008-2706-y

Oxygen diffusion in Ti–10Mo alloys measured by mechanical spectroscopy

Renata Abdallah Nogueira · Carlos Roberto Grandini · Ana Paula Rosifini Alves Claro

Received: 14 December 2007 / Accepted: 6 May 2008 / Published online: 13 August 2008

Abstract The addition of interstitial elements in metals, as titanium and its alloys, causes alterations in their mechanical properties, making them either softer or harder, for example. The internal friction measurements have been frequently used in order to verify the behavior of these interstitials atoms in metallic alloys. This paper presents the oxygen diffusion in Ti–10Mo alloy by the analysis of the mechanical relaxation spectra, in the temperature range of 350–600 K. The relaxation structure obtained was analyzed by means of the frequency dependence of the peak temperature and by using a simple mathematical treatment of the relaxation structure and the Arrhenius law.

Introduction

Combining mechanical strength and density, as well as high corrosion resistance, titanium alloys are an excellent material for applications in the aeronautical and automobile industry, in addition to being often used as a biomaterial [1–3]. The addition of interstitial elements in these metals leads to strong alterations in their mechanical properties, causing, for example, their softening or hardening [4].

The Ti–6Al–4V is the most used alloy for orthopedic implants. Even so, it is known that the aluminum causes neurological disorders and the vanadium is associated with enzymatic disturbances, among other problems [5, 6]. Thus, many researchers have been seeking alternatives to this titanium alloys, in attempt to obtain materials with similar (or higher) mechanical strength, smaller elasticity modulus, and better biocompatibility. The most promising are the ones presenting niobium, zirconium, molybdenum, and tantalum as alloy's elements, added to the titanium [7]. The Ti–10Mo (TM) alloy integrates a new class of titanium-based alloys, without aluminum and vanadium and with low values of the elasticity modulus (about 90 GPa), which becomes quite attractive for their employment as biomaterials [8]. In beta phase, this alloy presents bcc structure [9].

Metals having bcc structure receiving the addition of interstitial atoms—such as oxygen—undergo significant alterations in their physical properties, being able to dissolve large amounts of those elements, thus forming solid solutions. Titanium and some of its alloys have bcc structure, and understanding the interaction mechanisms between interstitial elements and titanium or its alloys is fundamental.

The study of interactions of heavy interstitial atoms present in metals with bcc structure began with Snoek's first work [10], in which he postulated that a stress-induced ordering of the interstitials gives rise to a peak in the mechanical relaxation (internal friction) spectra, afterwards known as Snoek's peak. By means of mechanical spectroscopy, it is possible to obtain information on diffusion, interstitial concentration, precipitation, solubility limit, interaction between interstitials and other imperfections of the crystalline lattice. The presence of substitutional solutes has a strong influence on the Snoek effect, resulting in the appearance of new relaxation peaks, and sometimes causing the suppression of the ordinary Snoek relaxation. Such features have been interpreted in terms of the lattice's

R. A. Nogueira · C. R. Grandini (✉)
UNESP, Grupo de Relaxações Anelásticas, 17.033-360 Bauru, SP, Brazil
e-mail: betog@fc.unesp.br

A. P. R. A. Claro
UNESP, Departamento de Materiais e Tecnologia, 12.516-410 Guaratinguetá, SP, Brazil

substitutional and interstitial complexing [11]. Internal friction is typically determined by damping mechanical oscillations and measured as a function of temperature. In the mechanical relaxation spectra, each species of interstitial solute atoms gives rise to a distinct Snoek's peak, and the temperature and position depend on the measurement frequency. This effect is very interesting because its peculiar parameters are directly related to the diffusion coefficient (*D*) of the interstitial solute.

This paper presents the oxygen diffusion in TM alloys using mechanical spectroscopy measurements. The results show anelastic relaxation spectra with the presence of a relaxation structure that was attributed to the stress-induced ordering of oxygen interstitial atoms around Ti and Mo of the alloy.

Experimental part

The used samples consist of polycrystals of the TM alloy, produced by arc melting in argon atmosphere [9]. The samples have square cross section, with dimension of 2.0 × 2.0 × 34 mm^3. In the as-received form (sample TM#1), it is in the β-phase, with bcc structure, as shown in Figs. 1 and 2. These measurements were made using a Rigaku model D/MAX-2100/PC, using Cu K_α radiation and a Leica Stereoscan 400 microscope.

In order to evaluate the effect of the interstitial elements in the anelastic properties of the TM alloy, an annealing and an oxygen charge were performed. In the case of the annealing, the temperature was increased up to 1,100 °C, at a heating rate of 10 °C/min, having remained in this temperature for 6 h it tends to cool up without a pre-established rate (furnace cooling) up to room temperature. Regarding the oxygen charge, the temperature was increased up to 800 °C, at a heating rate of 10 °C/min. At this temperature, a partial pressure of 1×10^{-5} Torr of oxygen was injected, having remained in these conditions for 30 min. Next, a fast cooling up to room temperature was performed. Both treatments were accompanied by a Residual Gas Analyzer, which is computer controlled, and verifies which elements occasionally exit from the sample during the abovementioned processes. Under these conditions, the quantity of oxygen in the sample, measured by the melt in inert gas and infra-red detection (HORIBA model EMGA-520 equipment), was (0.149 ± 0.005) wt.%. The samples were named TM#2 (after heat treatment) and TM#3 (after oxygen charge).

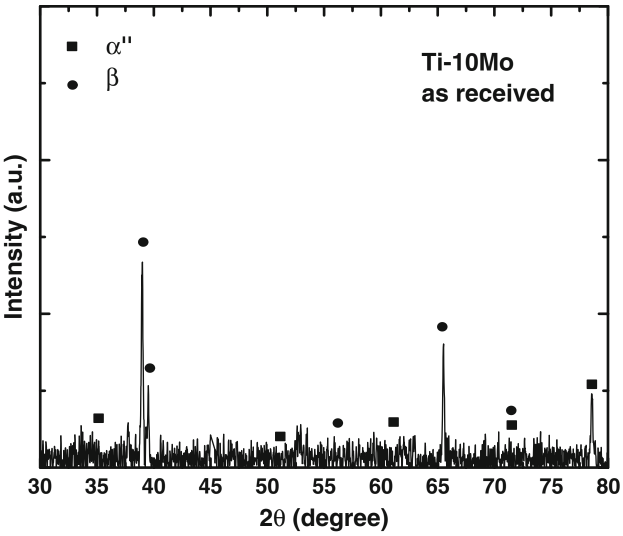

Fig. 1 X-ray diffractogram for the TM sample in the as-received condition

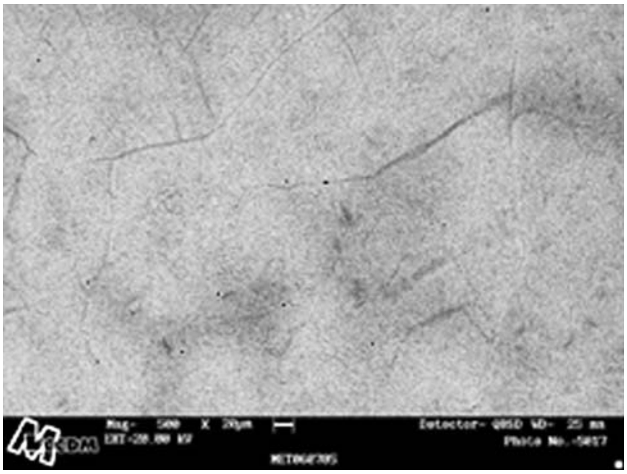

Fig. 2 SEM micrograph for the TM sample in the as-received condition

In order to study the oxygen diffusion, mechanical spectroscopy (internal friction and frequency) measurements were performed, using a torsion pendulum, operating at a temperature ranging from 90 to 700 K, at a frequency varying between 3 and 30 Hz, at a heating rate of ~1 K/min and under vacuum better than 10^{-6} Torr, to avoid sample contamination [12]. In the mechanical spectroscopy measurements, after an initial torque, the sample is placed to vibrate in its fundamental mode, which causes energy dissipation in a heat form, due to the internal friction. In the torsion pendulum, this energy dissipation by cycle is measured by the logarithmic decrement of the amplitude of system's free oscillations, that is, unless a constant, the own internal friction of the sample [11].

Results and discussions

Figure 3 shows a comparison among the anelastic spectra for the TM alloys, measured after heat treatment (sample

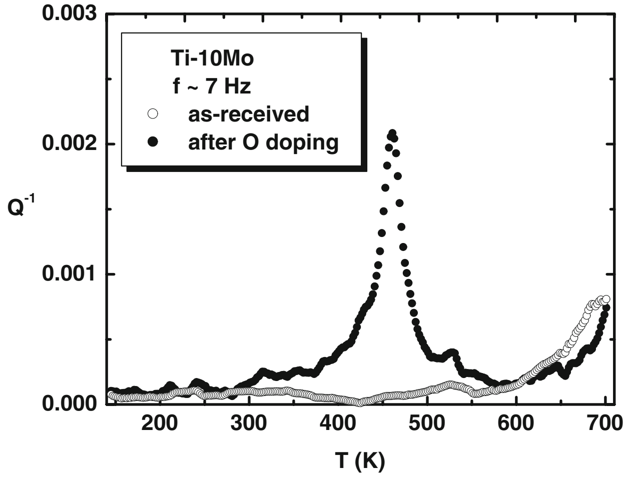

Fig. 3 Comparison between the anelastic spectra for the samples after heat treatment and after oxygen charge

TM#2) and after oxygen charge (sample TM#3), at a frequency of ~7 Hz. A relaxation structure of around 450 K only after the oxygen charge is verified. It can be observed that the spectrum of the sample measured after the heat treatment (used as background) possesses an exponential growing type [11]. This relaxation structure is thermally activated, as noted in Fig. 4. In a first approximation, this relaxation structure can be attributed to the stress-induced ordering of oxygen atoms around titanium and molybdenum atoms of the lattice.

Mechanical spectroscopy measurements have been frequently used to verify the behavior of interstitial atoms in alloys. Consequently, through them, information regarding imperfections in the crystalline lattice can be obtained, more specifically the diffusivity of these elements in the alloy [13–15]. The internal friction and frequency as function of the temperature, measured in the proximity of Snoek's peak, can be used to obtain information about the characteristics of point defect diffusion, its thermal activations, the formation of different point defects, and its redistribution under the effect of an external stress.

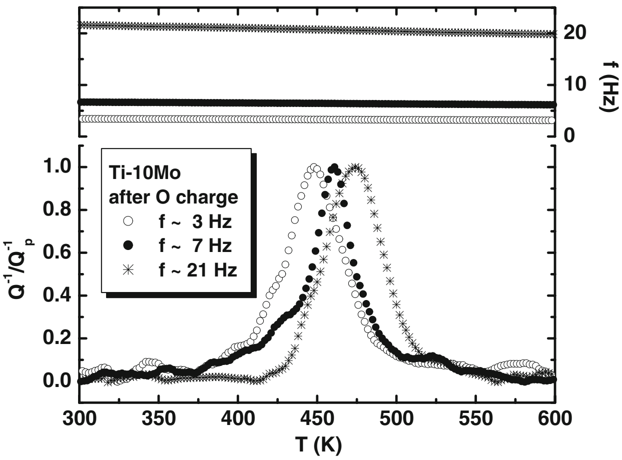

Fig. 4 Internal friction for the sample after oxygen charge, measured at different frequencies

For a material with bcc structure, the migration of the interstitial atoms is given by jumps among octahedral or tetrahedral sites, energetically equivalent. In the case of oxygen, these jumps occur among octahedral sites and the diffusion of these atoms is governed by the following expression [11]:

$$D = \frac{a_0^2}{36\tau}, \tag{1}$$

where D is the diffusion coefficient, a_0 the lattice parameter, and τ is the relaxation time.

If the relaxation process is thermally activated, the relaxation time can be written using Arrhenius' law and the diffusion coefficient can be obtained as a function of temperature:

$$D = D_0 \exp\left(-\frac{E}{kT}\right), \tag{2}$$

where τ_o is the fundamental relaxation time, E the activation energy, k the Boltzmann's constant, T the absolute temperature, and D_0 is the pre-exponential factor.

Assuming that the relaxation structure shown in Fig. 3 is composed by a single relaxation process due to the interaction of interstitial solutes and the metallic matrix, and that this relaxation process can be represented by Debye's peak, the basic equation for the internal friction for each relaxation process is given by [11]:

$$Q^{-1}(\omega\tau) = \Delta\frac{\omega\tau}{1 + (\omega\tau)^2}, \tag{3}$$

where Δ relaxation strength, τ corresponds to the relaxation time, and $\omega = 2\pi f$, f to the oscillating frequency of the system.

The position in temperature of the Snoek peak (for a given frequency f_p), T_p, is closely correlated with the activation energy, E. The maximum of internal friction described by Eq. 3 occurs at $\omega\tau = 1$, which gives, with Arrhenius' law, the relation between activation energy and peak temperature [11]:

$$\ln f_p = -\ln 2\pi\tau_0 - E/kT_{p.} \tag{4}$$

The peak temperatures of the observed peaks are plotted in Fig. 5. It can be observed that the points exhibiting a linear behavior in the frequency measured range and the activation energy and τ_0 obtained by the linear regression of the curve (correlation index of 0.984) were (1.30 ± 0.02) eV and $(1.24 \pm 0.05) \times 10^{-16}$ s, respectively.

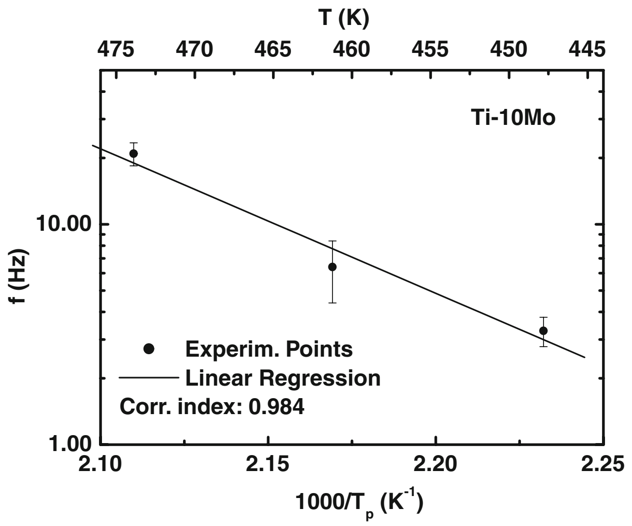

Fig. 5 Frequency as a function of peak temperature for the relaxation process observed in TM sample

Solving Eq. 3 for τ, it is obtained:

$$\tau = \frac{1}{\omega}\left[\frac{\Delta}{2Q^{-1}} \pm \sqrt{\left(\frac{\Delta}{2Q^{-1}}\right)^2 - 1}\right] \quad (5)$$

with [16]:

$$\Delta = \frac{2Q_p^{-1}T_p}{T}, \quad (6)$$

where Q_p^{-1} and T_p are the intensity and the temperature of the peak, respectively.

The relaxation time can be written as follows:

$$\tau = \frac{1}{\omega}\left[\frac{Q_p^{-1}T_p}{Q^{-1}T} \pm \sqrt{\left(\frac{Q_p^{-1}T_p}{Q^{-1}T}\right)^2 - 1}\right]. \quad (7)$$

Therefore, by plotting the τ logarithm as a function of the inverse of the temperature using the data presented in Fig. 4, a straight line can be obtained, as shown in Fig. 6. Using a linear regression, it was obtained the activation energy, E, and the fundamental relaxation time, τ_0, for the oxygen diffusion in the TM alloy. The obtained values are $\tau_0 = (2.59 \pm 0.02) \times 10^{-18}$ s and $E = (1.46 \pm 0.05)$ eV. From Eq. 1 and the lattice parameter obtained from X-ray measurements (shown in Fig. 1), it can be constructed the curve shown in Fig. 7. Using a linear regression the pre-exponential factor, D_0, and the activation energy, E, for the oxygen diffusion in the TM alloy can be obtained. The values found are $D_0 = (11.2 \pm 0.3) \times 10^{-4}$ cm^2/s and $E = (1.46 \pm 0.05)$ eV. From the results of frequency dependence of the peak temperature, the obtained value of D_0 is $(23.4 \pm 0.7) \times 10^{-4}$ cm^2/s.

The values of E and D_0 found in the literature are very controversy for the diffusion of oxygen in α titanium.

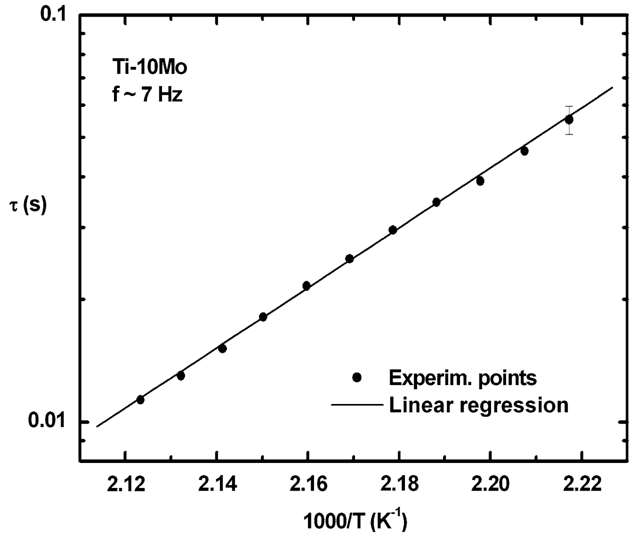

Fig. 6 Relaxation time as a function of temperature for the TM sample, measured at a frequency of around 7 Hz

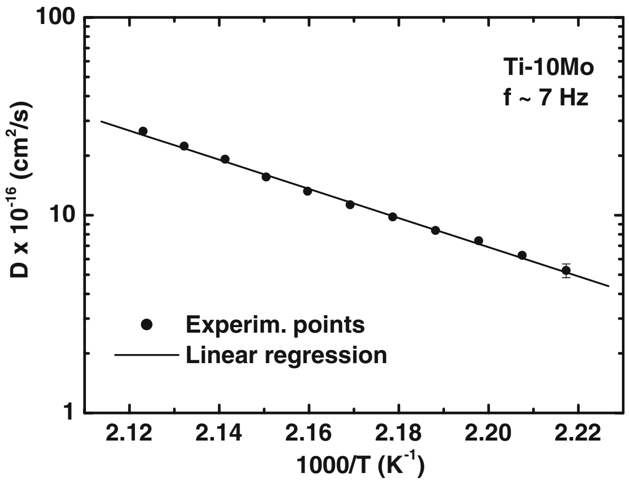

Fig. 7 Diffusion coefficient as a function of temperature for the TM sample, measured at a frequency of around 7 Hz

Tikhomirov and Dyachov [17] using oxidation and measurement of mass of the oxidized layer by weighing found 2.97 eV and 9.4×10^{-4} cm^2/s; Sokirianskii and Ignatov [18] using X-ray and microhardness found 2.25 eV and 16 cm^2/s; Rosa [19] using kinetics of displacement of the interface α/β found 2.11 eV and 0.778 cm^2/s; Kosfstad et al. [20] using X-ray and microhardness found 2.21 eV and 0.5 cm^2/s; Revyakin [21] using X-ray and microhardness, too, found 1.55 eV and 1.8×10^{-3} cm^2/s; Roe et al. [22] using microhardness found 1.45 eV and 5.08×10^{-3} cm^2/s; Hauffe [23] and Jenkis [24] using X-ray and microhardness, too, found 2.09 eV and 1.6 cm^2/s; Com-Nouguè [25] using proportioning of oxygen by nuclear reaction ^{16}O(d,p)^{17}O* found 1.35 eV and 1.32×10^{-4} cm^2/s; Feldman et al. [26] using oxidation, by determination of the oxygen mass in oxides according to the thickness, found 2.04 eV and 0.408 cm^2/s; David et al. [27, 28] using proportioning of oxygen by nuclear reaction $^{16}O(d,p)^{17}O^*$, too, found 2.08 eV and 0.45×10^{-4} cm^2/s; Roe et al. [22] found 2.98 eV and 3.14×10^{-4} cm^2/s and Güçlü et al. [29] found the activation energy in the range of 1.54–1.76 eV. These values were obtained in the temperature range of 900–1,400 K.

In the case of alloys, Niemeyer et al. [30] studied Nb-0.3 wt.%Ti using mechanical spectroscopy technique with frequency in the Hz range and found $E = 1.23$ eV for the Ti–O process; Cantelli and Szkopiak [31] studied Nb-1.0 at.%Ti using the same techniques and found $E = 1.23$ eV; Almeida et al [32] studied Nb-1.6 at.%Ti and found 1.23 eV for the same process and Lutz et al. [33] studied the Ti–6Al–4V alloys and found the activation energy in the range of 0.98–1.00 eV for the bulk and surface diffusion.

It can be observed a very disagree among the results previously published. According to Peterson [34], the use of internal friction measurements to study the oxygen diffusion in titanium varies as alloys elements are added. It is clear from the results above, where the activation energy of this process can vary from 1.35 to 2.98 eV for the addition of up to 10% of other elements. Another factor is that the peak can be composed by more than one relaxation process and in this case, the relaxation structure is decomposed into a distribution of relaxation times. Hence, the difference found between the values of E and D_0 reported in the paper for oxygen diffusion and the ones available in the literature for titanium containing oxygen is, in part, due to the fact that the relaxation structure is composed by more than one relaxation process. This explains the results obtained in this study.

Conclusions

Mechanical spectroscopy measurements were performed in samples of TM alloys, as well as in the as-received condition after oxygen doping.

In the as-received sample, no relaxation structure was observed. However, it was observed a thermally activated relaxation structure in the sample after doping. It was associated with the interstitial diffusion of oxygen atoms in a solid solution in the alloy.

The diffusion coefficient for the oxygen diffusion in the alloy was obtained by means of the frequency dependence of the peak temperature and by using a simple mathematical treatment of the relaxation structure and the Arrhenius law, i.e., the shape of Debye peak.

Acknowledgements The authors would like to thank the Brazilian agencies, FAPESP and CNPq, for their financial support.

References

1. Jafee RI, Promisel NE (1970) The science, technology and application of titanium. Pergamon Press, London
2. Donachie MJ (1988) Titanium—a technical guide. ASM, Ohio
3. Polmear IJ (1995) Light alloys, metallurgy of the light metals, 3rd edn. Edward Arnold, Great Britain
4. Souza AC, Grandini CR, Florêncio O (2008) J Mater Sci 43:1593. doi:10.1007/s10853-007-2324-0
5. Khan MA, Willians RL, Willians DF (1996) Biomaterials 17:2117. doi:10.1016/0142-9612(96)00029-4
6. Long M, Rack HJ (1998) Biomaterials 19:1621. doi:10.1016/S0142-9612(97)00146-4
7. Guo H, Enamoto M (2002) Acta Mater 50:929. doi:10.1016/S1359-6454(01)00392-5
8. Ho WF, Ju CP, Lin JHC (1999) Biomaterials 20:2115. doi:10.1016/S0142-9612(99)00114-3
9. Alves APR, Santana FA, Rosa LAA et al (2004) Mater Sci Eng C 24:693. doi:10.1016/j.msec.2004.08.013
10. Snoek JL (1939) Physica 6:591. doi:10.1016/S0031-8914(39)90061-3
11. Nowick AS, Berry BS (1972) Anelastic relaxation in crystalline solids. Academic Press, New York
12. Grandini CR (2002) Rev Bras Apl Vácuo 21:138
13. Florêncio O, Silva PS Jr, Grandini CR (2006) Diffus Defect Data A 258–260:137
14. Grandini CR, Silva LM, Almeida LH et al (2008) Diffus Defect Data A 273–276:256
15. Souza AC, Grandini CR, Florêncio O (2008) Diffus Defect Data A 273–276:261
16. Weller M (1981) Acta Metall 29:1047. doi:10.1016/0001-6160(81)90056-0
17. Tikhomitrov V, Dyachkov U (1967) Zh Prikl Khim 4:245
18. Sokirianskii L, Ignatov D (1969) Fiz Met Metalloved 28:287
19. Rosa CJ (1970) Metall Trans 1:2617
20. Kofstad P, Andersson PB, Krudtaa OJ (1961) J Less Common Met 3:89. doi:10.1016/0022-5088(61)90001-7
21. Revyakin AV (1961) Izv Akad Nauk SSSR 5:113
22. Roe WP, Palmer HR, Opie WR (1960) Trans ASM 52:191
23. Hauffe K (1965) Oxidation of metals. Plenum Press, New York
24. Jenkis AE (1954) J Inst Met 82:213
25. Com-Nouguè J (1972) Thèse, Paris-Sud, Paris
26. Feldman R, Déchamps M, Lehr P (1977) Métaux Corrosion Industrie 617:140
27. David D, Garcia EA, Lucas X, Beranger G (1979) J Less Common Met 65:51. doi:10.1016/0022-5088(79)90152-8
28. David D, Beranger G, Garcia EA (1983) J Eletroch Soc 130:1423. doi:10.1149/1.2119966
29. Güçlü FM, Çimenoglu H, Kayali ES (2006) Mater Sci Eng C 26:1367
30. Niemeyer TC, Grandini CR, Florêncio O (2005) Mater Sci Eng A 396:285
31. Cantelli R, Szkopiak ZC (1976) Appl Phys 9:153. doi:10.1007/BF00903952
32. Almeida LH, Niemeyer TC, Pires KCC et al (2004) Mater Sci Eng A 370:96
33. Lutz T, Gerlach JW, Mändl S (2007) Surf Coat Technol 201:6690. doi:10.1016/j.surfcoat.2006.09.102
34. Peterson NL (1961) Diffusion in refractory metals. Wadd Technical Report