

Activation Energy Measurement of Oxygen Ordering in a Nb-Ti Alloy by Anelastic Relaxation

T.C. Niemeyer^{a,b}, J.M.A. Gimenez^b, L.H. Almeida^b, C.R. Grandini^{b*}, O. Florêncio^c

^a Instituto de Física de São Carlos, Universidade de São Paulo, 13560-970 São Carlos - SP, Brazil

^b Departamento de Física, Universidade Estadual Paulista, 17033-360 Bauru - SP, Brazil

^c Departamento de Física, Universidade Federal de São Carlos, 13565-905 São Carlos - SP, Brazil

Received: November 13, 2000; Revised: February 25, 2002

Metals with bcc structure are able to dissolve large amounts of interstitial element atoms in the form of oxygen. These atoms diffuse through the lattice by jumping into octahedral sites with equivalent symmetry, causing strong alterations in the anelastic behavior. This paper reports on a study of Snoek relaxation in Nb-Ti alloys with oxygen in solid solution, based on internal friction as a function of temperature. The internal friction measurements were taken in a torsion pendulum operating at temperatures in the range of 350 to 650 K, with frequencies varying from 6 to 36 Hz. The results show relaxation spectra in which thermally activated relaxation peaks produced by the stress-induced ordering of oxygen atoms around niobium atoms of the metallic matrix were identified.

Keywords: *anelasticity, internal friction, diffusion, niobium-titanium alloys*

1. Introduction

Interest in the study of the interaction of interstitial solutes with metallic matrices began in the late 1930s with the work of Snoek¹, who postulated that carbon atoms dissolved interstitially in an α -iron matrix produced anelastic behavior, interacting with the metallic matrix through a relaxation process well known as stress-induced ordering. Since then, several studies have focused on gaining a better understanding of the mechanisms of this interaction, most of them based on the measurement of internal friction as a function of temperature, better known today as anelastic spectroscopy.

In recent decades, internal friction measurements have been used as a rich source of information on solutes interstitially diffused in metals and metallic alloys, since they provide information regarding diffusion, interstitial concentrations, solubility limits, precipitation phenomena, interaction between interstitials and other imperfections in the crystalline lattice²⁻⁷.

Today, more than fifty years after the discovery of the "Snoek Peaks", studies are still being made to clarify the relaxation mechanisms in pure metals^{8,9} and metallic alloys such as Nb-Ti^{10,11} and Nb-Zr^{12,13}. Our main objective with this work is the systematic study of anelastic relaxations caused by stress-induced ordering of heavy interstitial sol-

utes present in metallic matrices of niobium-based alloys, such as Nb-Ti, using internal friction measurements based on the torsion pendulum technique.

This paper discusses a Snoek relaxation study of Nb-Ti alloy samples, with oxygen dissolved in solid solution, using internal friction measurements as a function of temperature.

2. Experimental Part

The samples in question are polycrystals of a Nb-Ti alloy having 0.3% in weight of Ti (Nb - 0.3% Ti), produced by the Materials Engineering Department, Lorena Faculty of Chemical Engineering (FAENQUIL), by mechanical mixing of Nb and TiO₂ powders followed by cold isostatic pressing and high vacuum sintering¹⁰. The samples are cylinder-shaped, with a 1.3 mm diameter for 45 mm of useful length. Table 1 gives the chemical composition of the sample used in this study.

Internal friction and oscillation frequency measurements were taken using an inverted torsion pendulum of the Kê type¹⁴, operating in the temperature range of 100 to 700 K and an oscillation frequency of 6.0 to 36.0 Hz. The measurements were taken in a vacuum close to 10⁻⁴ mBar, with a heating rate of approximately 1.0 K/min. The maximum

*e-mail: betog@fc.unesp.br

Trabalho apresentado no 14^o CBECIMAT, Águas de São Pedro, Dezembro de 2000.

Table 1. Chemical composition of the Nb - 0.3% Ti alloy used in this work.

	O	N	Al	Fe	Cu	Si
Maximum Contents (wt %)	0.041	0.004	0.013	0.005	0.002	0.004

deformation suffered by the samples during measurement was 10^{-5} .

To measure the internal friction, the sample is subjected to vibration in its fundamental mode (free or forced vibrations), which causes the dissipation of energy in the form of heat produced by internal friction. This dissipation can be measured direct or indirectly. In the case of the torsion pendulum, the dissipation of energy per cycle is measured through the logarithmic decrement of the amplitude of the free oscillations of the pendulum¹⁵, which is written as:

$$Q^{-1} = \frac{1}{N} \ln \frac{A_o}{A_N} \quad (1)$$

where N is the number of oscillations during which the amplitude decreases from A_o to A_N .

An anelastic relaxation process gives rise to a peak in the internal friction spectrum as a function of the temperature and a step in the Elasticity Modulus. The height of the internal friction peak and the amplitude of the step in the modulus are correlated with the concentration of the bodies undergoing relaxation while the peak's position is determined by the bodies' mobility.

Oscillation amplitude damping data were collected automatically, using a laser beam reflected by a mirror placed on the axis of the pendulum and incident on two photodiodes connected to a microcomputer¹⁶.

3. Results and Discussion

Figure 1 illustrates the internal friction and relative frequency variation (elasticity modulus) as a function of temperature for a sample of the Nb-0.3 wt % Ti alloy with 0.04 wt % of oxygen in solid solution, measured with a frequency of 6 Hz. The figure clearly shows the presence of a relaxation peak around 475 K.

The same phenomena are observed in Figs. 2 to 4, which show the internal friction and relative variation of frequency as a function of temperature for the same sample, now measured at frequencies of 12, 14 and 36 Hz, respectively.

A possible explanation for this relaxation peak is the stress-induced ordering of oxygen atoms located interstitially in octahedral sites of the lattice around niobium atoms of the metallic matrix.

The first indication underpinning the validity of this as-

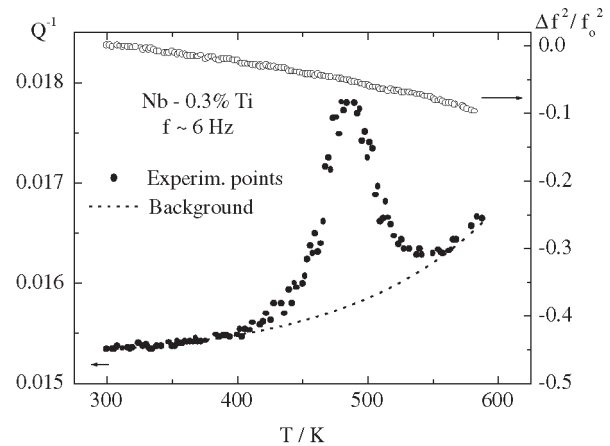


Figure 1. Internal friction (●) and elasticity modulus (○) as a function of temperature for a Nb-0.3 wt % Ti sample with 0.04 wt % of oxygen, measured at a frequency of 6 Hz. The dashed line indicates the background.

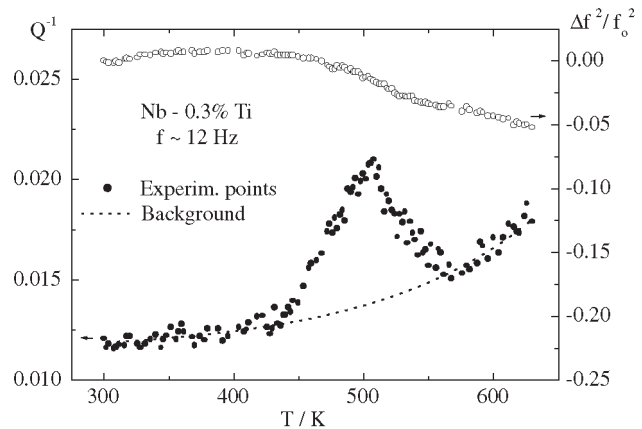


Figure 2. Internal friction (●) and elasticity modulus (○) as a function of temperature for a sample of Nb-0.3 wt % Ti with 0.04 wt % of oxygen, measured at a frequency of 12 Hz. The dashed line indicates the background.

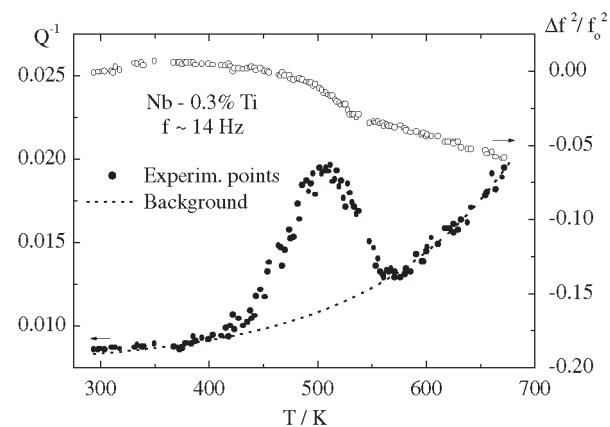


Figure 3. Internal friction (●) and elasticity modulus (○) as a function of temperature for a sample of Nb-0.3 wt % Ti with 0.04 wt % of oxygen, measured at a frequency of 14 Hz. The dashed line indicates the background.

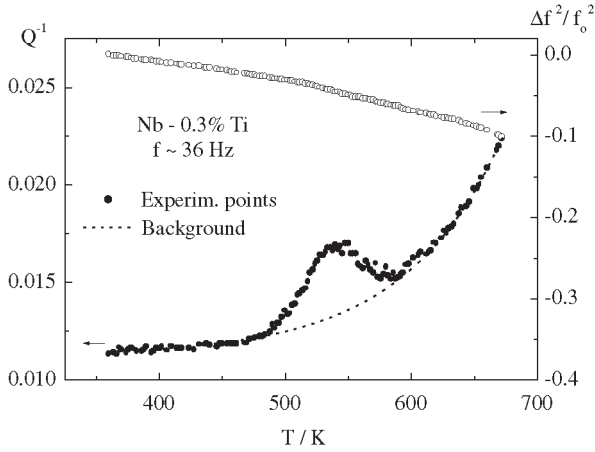


Figure 4. Internal friction (●) and elasticity modulus (○) as a function of temperature for a sample of Nb-0.3 wt % Ti with 0.04 wt % of oxygen, measured at a frequency of 36 Hz. The dashed line indicates the background.

sumption is that the relaxation peak is thermally activated. Figure 5 shows the influence of frequency on internal friction measurements as a function of temperature. As can be seen in the figure, a displacement of the relaxation structure to a higher temperature occurs with the increase in frequency, demonstrating that the process is thermally activated. If the process is, in fact, thermally activated, then it satisfies Arrhenius' equation¹⁵:

$$\tau = \tau_0 \exp(E/kT) \quad (2)$$

where E is the activation energy and τ_0 is the jump rate of the relaxation process.

Thus, the internal friction and frequency measured in the neighborhood of the Snoek peaks constitute a useful tool to obtain the activation energy and jump rate of the relaxation process based on Arrhenius' Law. The basic condition for the occurrence of a relaxation peak is:

$$\omega \tau = 1 \quad (3)$$

where τ is the relaxation time of the process, $\omega = 2\pi f$ is the angular frequency and f is the oscillation frequency of the pendulum.

Hence:

$$\ln f = -\ln 2\pi\tau_0 - E/kT_p \quad (4)$$

where T_p is the peak temperature.

By plotting a graph of the frequency logarithm as a function of the inverse of the temperature one can obtain the activation energy and the relaxation time of the process. Fig. 6 contains such a graph.

A linear regression analysis was used to find the parameters for the straight line shown in Fig. 6, whose linear coefficient is 22.86 s^{-1} and angular coefficient -13.22 .

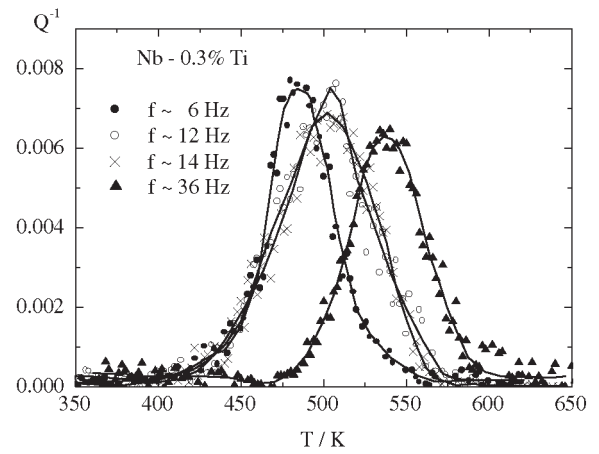


Figure 5. Influence of the frequency on the relaxation process due to interstitial impurities in the Nb-0.3 wt % Ti sample.

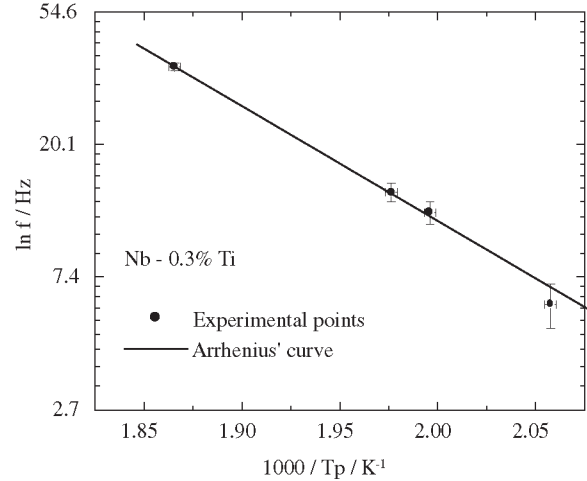


Figure 6. Logarithm of the frequency as a function of the inverse of the peak temperature for the Nb-0.3 wt % Ti sample.

In this case, the activation energy and the jump rate are:

$$E = (1.14 \pm 0.09) \text{ eV} \quad \tau_0^{-1} = (5.33 \pm 0.02) \times 10^{10} \text{ s}^{-1}$$

These results are in reasonable agreement with previously published results^{2,5,8,10}, reinforcing our initial supposition.

For a definitive confirmation of this assumption, we will admit that the anelastic relaxation represented by the peak in the internal friction spectrum is governed by one relaxation process, in which case the basic equation for the internal friction is given by¹⁵:

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

where Δ is the relaxation strength, τ is the relaxation time and $\omega = 2\pi f$, f is the oscillation frequency of the pendulum.

According to Weller *et al.*⁶, Δ can be written as:

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

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

Figures 7 to 10 show the spectra of internal friction as a function of temperature for the Nb-0.3 wt% Ti sample measured, respectively, at the frequencies of 6, 12, 14 and 36 Hz. The full curve of the figures represents a Debye peak, which can be obtained through a combination of equations (5) and (6) and Arrhenius' Law (2)¹⁵, as follows:

$$Q^{-1} = \frac{2Q_p^{-1}T_p}{T} \operatorname{sech}\left[\frac{E}{k}\left(\frac{1}{T_p} - \frac{1}{T}\right)\right] \quad (7)$$

The relaxation parameters for the Nb-O process obtained by this procedure are given in Table 2.

The figures show a good congruence between the experimental points and the theoretical curve in the region of the peak, confirming our initial supposition that the relaxation process studied here derives from the stress-induced ordering of oxygen atoms around niobium atoms in the metallic matrix (Nb-O process).

A critical analysis of Table 2 leads one to conclude that the results obtained in this study are in good agreement with those presented in the literature and that the relaxation process in question really originates from the stress-induced ordering of oxygen atoms around niobium atoms in the metallic matrix. The low concentrations of oxygen and titanium are still insufficient for a proper visualization of the relaxation process produced by the stress-induced ordering of oxygen atoms around titanium atoms in the metallic matrix.

Table 2. Relaxation parameters for the Nb-O process.

Frequency (Hz)	Temperature (K)	Activation Energy (eV)	Ref.
		1.14	This work (Fig.6)
6	485	1.15	This work (Fig. 7)
12	501	1.15	This work (Fig. 8)
14	503	1.15	This work (Fig.9)
36	537	1.15	This work (Fig.10)
1.0	425	1.15	[2]
2.9	440	1.15	[6]
1.3	430	1.15	[10]
1.0	430	1.15	[11]
3.5	442	1.17	[17]

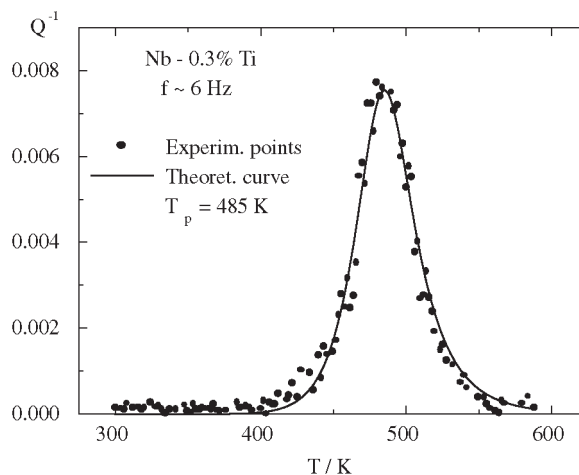


Figure 7. Internal friction as a function of temperature for a sample of Nb-0.3 wt % Ti with 0.04 wt % of oxygen, measured at a frequency of 6 Hz, analyzed as a Debye peak.

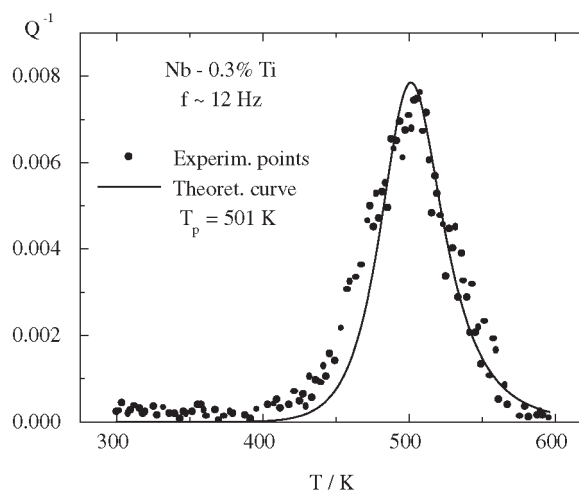


Figure 8. Internal friction as a function of temperature for a sample of Nb-0.3 wt % Ti with 0.04 wt % of oxygen, measured at a frequency of 12 Hz, analyzed as a Debye peak.

The intensity of the constituent Debye peaks allowed for the oxygen concentration in the sample to be estimated at 0.03%, based on the Elastic Dipole Theory developed by Nowick¹⁵ and on the work of Povolo and Lambri¹⁸.

4. Conclusions

Based on measurements of internal friction as a function of temperature, we analyzed samples of Nb-0.3 wt % Ti with oxygen in solution solid dissolved interstitially in the metallic matrix.

The resulting spectra showed the presence of relaxation structures associated to the relaxation process, caused by stress-induced ordering of oxygen atoms around niobium

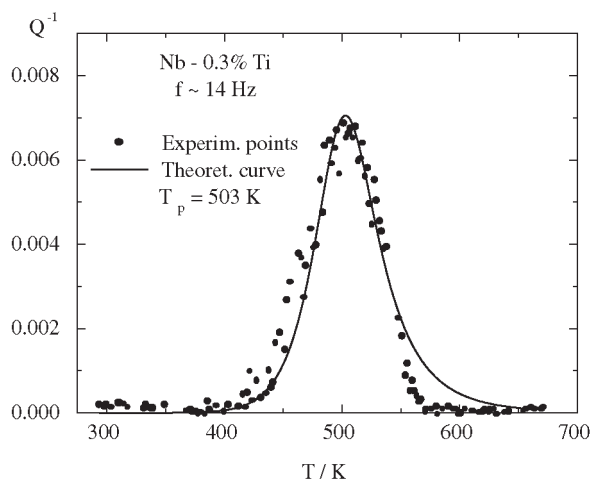


Figure 9. Internal friction as a function of temperature for a sample of Nb-0.3 wt % Ti with 0.04 wt % of oxygen, measured at a frequency of 14 Hz, analyzed as a Debye peak.

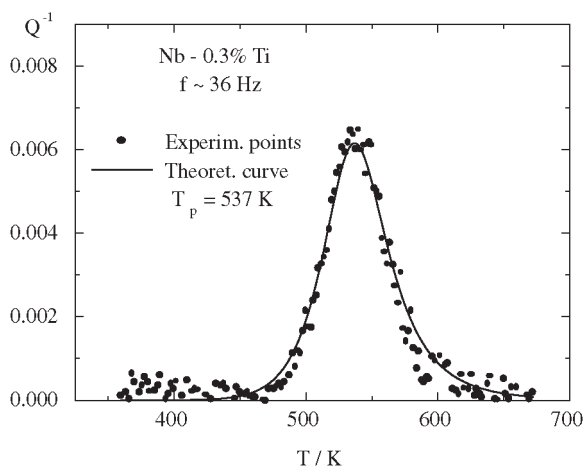


Figure 10. Internal friction as a function of temperature for a sample of Nb-0.3 wt % Ti with 0.04 wt % of oxygen, measured at a frequency of 36 Hz, analyzed as a Debye peak.

atoms (Nb-O process).

Through a method of computational analysis of the peaks, called the Successive Subtractions Method, a value of 1.15 eV was found for the activation energy of the thermally activated jumps (diffusion) of oxygen atoms around niobium atoms in the metallic matrix. This value was very close to those reported in the literature, confirming the usefulness of the torsion pendulum technique in studies on mechanical relaxations in materials.

The oxygen concentration in solid solution, which was found to be 0.03 in %, was estimated based on the height of

the Debye peaks.

Acknowledgements

The authors thank FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FUNDUNESP (Fundação para o Desenvolvimento da UNESP) for their financial support of this work.

References

1. Snoek, J.L. *Physica*, v. 8, p. 711-733, 1941.
2. Ahmad, M.S.; Szkopiak, Z.C. *J. Phys. Chem. of Solids*, v. 31, p. 1799-1804, 1970.
3. Heulin B.C.R. *Acad. Sc. Paris*, v. 273, p. 349-354, 1972.
4. Indrawirawan H.; Brasche L.J.; Owen C.V.; Rehbein D.K.; Carlson O.N.; Peterson D.T.; Buck O.J. *Phys. Chem. Solids*, v. 48, p. 535-539, 1987.
5. Haneckzok G.; Weller M. *J. Less-Common Metals*, v. 159, 269-276, 1990.
6. Weller M.; Haneckzok G.; Diehl J. *Phys. Stat. Sol. (b)*, v. 172, p. 145-159, 1992.
7. Haneckzok G.; Weller M.; Diehl J. *Phys. Stat. Sol. (b)*, v. 172, p. 557-572, 1992.
8. Grandini C.R.; Botta F^o W.J.; Florêncio O.; Tejima H.; and Jordão J.A.R. *J. Alloys Comp.*, v. 211/212, p. 226-228, 1994.
9. Haneckzok G. *Phil. Mag. A*, v. 78, p. 845-855, 1998.
10. Grandini C.R.; Ferreira L.E.C.; Sandim H.R.Z.; Florêncio O.; Tejima H.; Jordão J.A.R. *J. Phys. IV*, v. 6, p. 135-138, 1996.
11. Florêncio O.; Botta F^o W.J.; Grandini C.R.; Tejima H.; Jordão J.A.R. *J. Alloys Comp.*, v. 211/212, p. 37-40, 1994.
12. Botta F^o W.J.; Florêncio O.; Grandini C.R.; Tejima H.; Jordão J.A.R. *Acta Metall. Mater.*, v. 38, p. 391-396, 1990.
13. Ritchie G.; Pan Z.L. *Phil. Mag. A*, v. 63, p. 1105-1113, 1991.
14. Kê T.S. *Phys. Rev.*, v. 71, p. 533-546, 1947.
15. Nowick A.S.; Berry B.S., *Anelastic Relaxation in Crystalline Solids*, Academic Press, New York, USA, 1972.
16. Gimenez J.M.A.; Rezende R.; Niemeyer T.C.; China J.P.R.; Pintão C.A.F.; Grandini C.R.; Florêncio O. *Revista Brasileira de Aplicações de Vácuo*, v. 19, p. 33-35, 2000.
17. Grandini C.R.; Scalvi R.M.F.; Oliveira A.R.G.; Florêncio O.; Tejima H.; Jordão J.A.R. *Revista Brasileira de Física Aplicada e Instrumentação*, v. 10, p. 133-138, 1995.
18. Povolo F.; Lambri O.A. *J. Alloys Comp.*, v. 211/212, p. 41-44, 1994.