

M.L. NÓ*, L. DIRAND*, A. DENQUIN**, J. SAN JUAN***,#

INTERNAL FRICTION AND DYNAMIC MODULUS IN ULTRA-HIGH TEMPERATURE Ru-Nb FUNCTIONAL INTERMETALLICS

TARCIE WEWNĘTRZNE I MODUŁ DYNAMICZNY W BARDZO WYSOKO TEMPERATUROWYCH FUNKCJONALNYCH ZWIĄZKACH MIĘDZYMETALICZNYCH Z UKŁADU Ru-Nb

In the present work we have studied the high-temperature shape memory alloys based on the Ru-Nb system by using two mechanical spectrometers working in temperature ranges from 200 to 1450°C and -150 to 900°C. We have studied internal friction peaks linked to the martensitic transformations in the range from 300 to 1200°C. In addition, we have evidenced another internal friction peak at lower temperature than the transformations peaks, which apparently exhibits the behaviour of a thermally activated relaxation peak, but in fact is a strongly time-dependent peak. We have carefully studied this peak and discussed its microscopic origin, concluding that it is related to the interaction of some structural defects with martensite interfaces. Finally, we perform a complete analysis of the whole internal friction spectrum, taking into account the possible relationship between the time-dependent peak and the martensitic transformation behaviour.

Keywords: internal friction, Ruthenium-Niobium, martensitic transformation, shape memory alloys

W niniejszej pracy badano wysokotemperaturowe stopy z pamięcią kształtu z układu Ru-Nb, przy użyciu dwóch spektrometrów mechanicznych pracujących w zakresach temperatur od 200 do 1450°C i -150 do 900°C. Zbadano piki tarcia wewnętrznego związane z przemianami martenzytycznymi w zakresie od 300 do 1200°C. Ponadto, wykazano występowanie innego piku tarcia wewnętrznego przy niższej temperaturze niż pików przemiany, który ma cechy aktywowanego termicznie piku relaksacji, ale w rzeczywistości jest to pik silnie zależny od czasu. Dokładnie zbadano ten pik i omówiono jego pochodzenie w mikro skali, stwierdzając, że jest to związane z oddziaływaniem niektórych wad strukturalnych z granicami martenzytu. Na koniec, wykonano kompletną analizę całego spektrum wewnętrznego tarcia, biorąc pod uwagę możliwość związku między pikiem zależnym od czasu i zachowaniem przemiany martenzytycznej.

1. Introduction

Shape memory alloys (SMA) are functional intermetallics that can perform both sensing and actuating functions thanks to a reversible first order phase transition characterized mainly by an atomic shearing of the lattice planes from the high temperature and high symmetry phase, i.e., austenite, to the low temperature and lower symmetry phase called martensite. In SMA the transition between both phases can be induced thermally or by the application of a stress promoting crystallographic shearing during the transformation, and consequently the shape memory and superelastic properties are controlled by the behaviour of this thermo-elastic martensitic transformation (MT), see Ref. [1,2] for a general overview. The most developed and commercially available SMA are binary Ti-Ni alloys, which unfortunately have transformation temperatures limited to below 100°C. However, there are many potential applications requiring high temperature SMA

and several families of materials have been developed with transformation temperatures between 100°C and 600°C, as recently reviewed by Ma et al. [3]. Nevertheless there are very few potential candidates to fulfil the requirements to be used above 600°C, in hot areas of aero-engines and aerospace devices, which constitutes a scientific and technological challenge. Indeed, at present only the Ti-Pt(Ir) [4-7], Ru-Nb [8-13] and Ru-Ta [8,12-15] systems seem to be able of operating in the temperature range from 600 to 1200°C, and can be considered as ultra-high temperature SMA.

The present work is focused on Ru-50Nb (at.%) with the highest transformation temperatures in this system and exhibiting two successive martensitic transformations from β austenite, cubic B2 ordered (Pm $\bar{3}$ m), to a tetragonal β' martensite (P4/mmm) and then from β' to another monoclinic β'' martensite (P2/m) at lower temperature. The lattice parameters of these phases can be found in the literature [9,16,17].

* DPT. FISICA APLICADA II, FACULTAD DE CIENCIA Y TECNOLOGÍA, UNIVERSIDAD DEL PAÍS VASCO, UPV/EHU, APTDO 644, 48080 BILBAO, SPAIN

** ONERA, 29 AVENUE DE LA DIVISION LECLERC, F-92322 CHÂTILLON CEDEX, FRANCE

*** DPT. FISICA MATERIA CONDENSADA, FACULTAD DE CIENCIA Y TECNOLOGÍA, UNIV. DEL PAÍS VASCO, UPV/EHU, APTDO 644, 48080 BILBAO, SPAIN

Corresponding authors: maria.no@ehu.es, jose.sanjuan@ehu.es

2. Experimental

Ru-Nb alloys were produced from commercially pure elements by arc-melting under an argon atmosphere and re-melted several times to ensure the ingot compositional homogeneity [17]. Then the material was solid solution treated in vacuum at 1673 K for 5.7×10^5 s to eliminate any compositional gradient from dendritic solidification. The ingot was electro-spark machined and final samples were mechanically polished allowing the observation of a grain size of about 500 μm . The microstructure of the martensite was characterized at room temperature by scanning electron microscopy in back-scattered mode at 10 kV in a JEOL 7000F. The microstructure of the monoclinic β'' martensite, constituted mainly by shelf-accommodated groups of variants, is shown in Fig. 1. To study the martensitic transformation as a function of temperature the internal friction (IF) and dynamic shear modulus (DSM) were measured in two mechanical spectrometers based on a forced inverted torsion pendulum working in sub-resonant mode between 300-1800 K and 90-1200 K respectively, at different frequencies from 10^{-3} Hz to 3 Hz [18,19]. Measurements were performed in high vacuum, $\approx 10^{-5}$ mbar, to avoid oxidation of the sample.

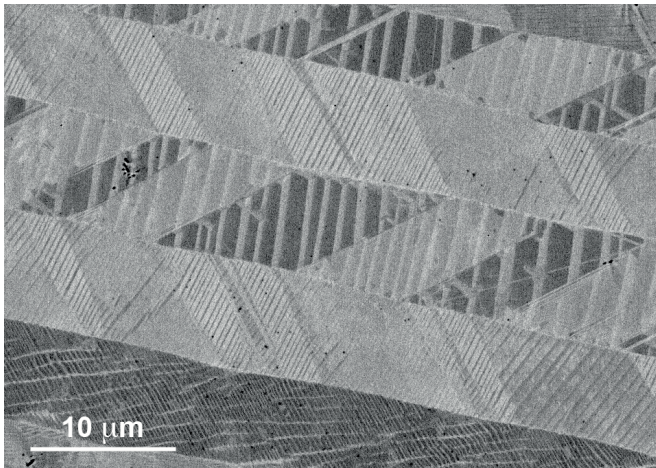


Fig. 1. Scanning electron micrograph of monoclinic martensite in Ru-50Nb SMA

3. Results

Internal friction and dynamic shear modulus curves during cooling and heating between 600 K and 1330 K were measured at 0.1 Hz with a heating/cooling rate of 1 K/min and an oscillating amplitude of $\varepsilon_0 = 10^{-5}$. The results are shown in Fig. 2 where sharp peaks are observed at 1158 K and 1027 K during cooling and at 1171 K and 1046 K during heating, corresponding to the forward (TP_F) and reverse (TP_R) martensitic transformations from β - β' and β' - β'' respectively. Taking as reference the peak temperature for the β - β' MT, our results agree quite well with those from the literature measured by dilatometry and differential thermal analysis (DTA): 1159 K [11,17] and 1158 K [8] for TP_F as well as 1172 K [11,17] and 1168 K [8] for TP_R . The general behaviour of the IF spectra can be analysed through the proposed models for MT [20-23]. One interesting point that can be noticed in Fig. 2 is the

clear softening of the dynamic shear modulus just before and during the martensitic transformation, which is recovered after the transformation. The drop of the dynamic shear modulus between 1300 K and 1180 K is a clear evidence of a pre-martensitic softening of the elastic constants in β phase, which has been discussed in previous work [24].

It should also be noted that the softening of the dynamic shear modulus is observed in Fig. 2 not only for the β - β' transformation but also for the β' - β'' transformation, which gives a clear indication of the thermo-elastic nature of these martensitic transformations. In addition a broad peak P_{LT} , at lower temperature than the β' - β'' transformation peak, is observed in Fig. 2. This peak is rather unexpected because such an anomaly has never been reported by dilatometry [8] and DTA [11,17]. Consequently we may disregard the possibility of attributing it to a martensitic transformation and it may be associated to a relaxation process linked to defects or the mobility of interfaces.

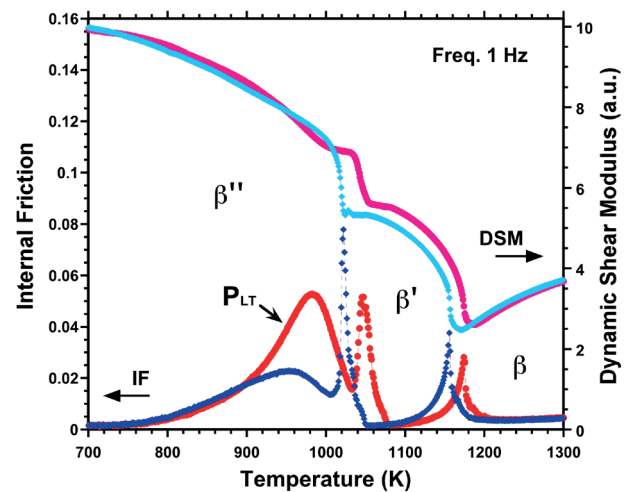


Fig. 2. Internal friction spectra and dynamic shear modulus variation curves (at 1 Hz) during heating (red & magenta dots) and cooling (blue & cyan diamonds). The sharp peaks of both transformations β - β' and β' - β'' and the low temperature peak P_{LT} are shown

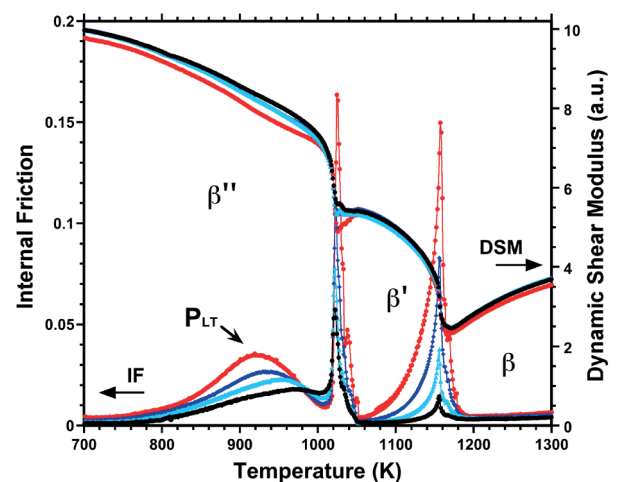


Fig. 3. Internal friction and dynamic modulus measured during cooling, for different frequencies: 0.1 Hz (red dots), 0.3 Hz (blue diamonds), 1 Hz (cyan triangles) and 3 Hz (black dots), with the same cooling rate of 1 K/min

To elucidate this problem, the IF and DSM have been measured at different frequencies between 3 Hz and 0.1 Hz and in Fig. 3 the corresponding cooling runs are plotted. In this series of spectra we may also observe that the strength of both transformation peaks β - β' and β' - β'' exhibit a dependence on $1/\omega$ according to the dependence on \dot{T}/ω predicted by the original model of Gremaud et al. [25]. This behaviour is characteristic of thermo-elastic martensitic transformations, being verified on many SMA, and this fact supports the idea of the thermo-elastic nature of both martensitic transformations β - β' and β' - β'' , as indicated by the softening of the dynamic shear modulus. In what concerns the low temperature peak P_{LT} , internal friction spectra shown in Fig. 3 indicate a shift of the temperature of the maximum with frequency as expected for a relaxation process. We may advance the idea that the apparent activation enthalpy measured from the temperature shift is too high to be attributed to a relaxation process with some specific physical meaning [26]. In fact, the P_{LT} peak is not a real relaxation peak because it disappears at constant temperature exhibiting strong time-dependence. Indeed the internal friction and dynamic shear modulus are plotted in Fig. 4 at 1 Hz during heating up to 962 K (close to the maximum of P_{LT} peak). Following this, both curves are measured as a function of time at constant temperature. The strong decrease of the IF can be interpreted as a decrease of the number of the relaxing units giving rise to IF, and the time-evolution of the DSM provides evidence of a simultaneous hardening as a function of time.

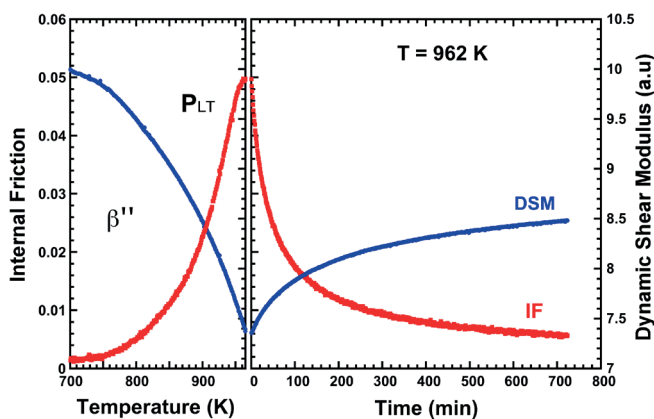


Fig. 4. Internal friction (red dots) and dynamic shear modulus evolution (blue dots) during heating (1 K/min) from 600 K up to 962 K (the temperature of the maximum of the P_{LT} peak), and then holding isothermally 12 h at this temperature. The frequency is 1 Hz

4. Discussion

The softening of the dynamic shear modulus just before and during both martensitic transformations β' and β'' , is a good indication of their thermo-elastic character. This is confirmed by recent results on internal friction measured as a function of the temperature rate and the oscillation frequency [27], which confirm an exceptional good fitting to the Gremaud model [25]. In light of obtained results the doubts on the intrinsic thermo-elastic character of the martensitic transformation in Ru-Nb shape memory alloys are mitigated, and the reason of the poor

strain recovery, particularly during the β'' transformation, should be attributed to extrinsic effects linked to the martensite interface mobility. Taking into account that the strength of the P_{LT} peak is completely regenerated when heating just above A_f of the β' - β'' martensitic transformations [27], a relationship between the peak P_{LT} and this transformation seems to be clear. In light of the present results a mechanism of pinning of the β'' martensite interfaces by point defects, mobile in the temperature range from 800 to 1000 K, is proposed. At this point it is difficult to determine the nature of such point defects, but our samples as well as other Ru-50Nb alloys described in the literature [8,11] are expected to contain some hundreds ppm of substitutional impurities and about 200 to 700 ppm of oxygen, which could constitute mobile defects able to migrate towards the interfaces of the martensite. The above interpretation is consistent with the observed dependence on time and the disappearance of β'' interfaces during the reverse transformation β'' - β' , which will re-dissolve in solid solution the point defects pinned at the interfaces, regenerating the P_{LT} peak. Further work is in progress to analyse the behaviour of the P_{LT} peak, in particular the kinetics of the internal friction and modulus evolution, in order to obtain precise information about the mechanism of interface pinning and the nature of the mobile point defects. This issue is out of the scope of the present paper and will be discussed in more detail elsewhere [27].

5. Conclusions

Internal friction and dynamic modulus have been measured in Ru-50Nb (at.%) intermetallic alloy. We may conclude that both martensitic transformations β - β' and β' - β'' in Ru-50Nb SMA exhibit a sharp internal friction peak and a dynamic modulus softening evidencing a clear thermoelastic behaviour. The β' - β'' transformation is affected by interface pinning effect caused by point defects, giving place to the time-dependent internal friction peak P_{LT} in β'' martensite phase.

Acknowledgements

This work has been supported by the Spanish Ministry, MINECO, project MAT2012-36421 and the CONSOLIDER-INGENIO 2010 CSD2009-00013, by the Consolidated Research Group IT-10-310 from the Education Dpt., and by project ETORTEK ACTIMAT from the Industry Dpt. of the Basque Government.

REFERENCES

- [1] Shape Memory Materials, edited by K. Otsuka and C.M. Wayman, Cambridge University Press, Cambridge, 1998.
- [2] Shape Memory and Superelastic Alloys, 2011, edited by K. Yamauchi, I. Ohkata, K. Tsuchiya and S. Miyazaki, Woodhead Publishing, Cambridge, 2011.
- [3] J. Ma, I. Karaman, R.D. Noebe, High temperature shape memory alloys, *Int. Mat. Rev.* **55**, 257-315 (2010).
- [4] T. Biggs, M.B. Cortie, M.J. Witcomb, L.A. Cornish, Martensitic transformations, microstructure, and mechanically workability

- of TiPt, *Metall. Mater. Trans. A* **32**, 1881-1886 (2001)
- [5] Y. Yamabe-Mitarai, T. Hara, H. Hosoda, Phase transformation of B2-PtTi with Ir, *Mat. Sci. For.* **426**, 2267-2272 (2003)
- [6] Y. Yamabe-Mitarai, T. Hara, S. Miura, H. Hosoda, Mechanical properties of Ti-50(Pt,Ir) high-temperature shape memory alloys, *Mater. Trans.* **47**, 650-657 (2006).
- [7] Y. Yamabe-Mitarai, T. Hara, S. Miura, H. Hosoda, Shape memory effect and pseudoelasticity of TiPt, *Intermetallics* **18**, 2275-2280 (2010).
- [8] R.W. Fonda, H.N. Jones, R.A. Vandermeer, The shape memory effect in equiatomic TaRu and NbRu alloys, *Scripta Mater.* **39**, 1031-1037 (1998).
- [9] R.W. Fonda, H.N. Jones, Microstructure, crystallography, and shape memory effect in equiatomic NbRu, *Mat. Sci. Eng. A* **273-275**, 275-279 (1999).
- [10] X. Gao, W. Cai, Y.F. Zheng, L.C. Zhao, Martensitic transformation and microstructure in Nb-Ru-Fe shape memory alloys, *Mat. Sci. Eng. A* **438-440**, 862-864 (2006).
- [11] K. Chastaing, A. Denquin, R. Portier, P. Vermaut, High-temperature shape memory alloys based on the RuNb system, *Mat. Sci. Eng. A* **481-482**, 702-706 (2008).
- [12] A. Manzoni, K. Chastaing, A. Denquin, P. Vermaut, R. Portier, Shape recovery in high temperature shape memory alloys based on the Ru-Nb and Ru-Ta systems, *ESOMAT-2009*, 05021 (2009).
- [13] A. Manzoni, K. Chastaing, A. Denquin, P. Vermaut, J. Van Humbeeck, R. Portier, The effect of Fe additions on the shape memory properties of Ru-based alloys, *Scripta Mater.* **64**, 1071-1074 (2011)
- [14] R.W. Fonda, R.A. Vandermeer, Crystallography and microstructure of TaRu, *Phil. Mag. A* **76**, 119-133 (1997).
- [15] Z. He, J. Zhou, Y. Furuya, Effect of Ta content on martensitic transformation behavior of RuTa ultrahigh temperature shape memory alloys, *Mat. Sci. Eng. A* **348**, 36-40 (2003).
- [16] S.M. Shapiro, G. Xu, G. Gu, J. Gardner, R.W. Fonda, Lattice dynamics of the high-temperature shape memory alloy Nb-Ru, *Phys. Rev. B* **73**, 214114 (2006).
- [17] K. Chastaing, PhD These, Étude d'alliages à mémoire de forme base Ru pour applications hautes températures, Université Pierre et Marie Curie, Paris, 2007.
- [18] I. Gutiérrez-Urrutia, M.L. Nó, E. Carreño-Morelli, B. Guisolan, R. Schaller, J. San Juan, High performance very low frequency pendulum, *Mat. Sci. Eng. A* **370**, 435-439 (2004).
- [19] P. Simas, J. San Juan, R. Schaller, M.L. Nó, High-temperature mechanical spectrometer for internal friction measurements, *Key Eng. Mater.* **423**, 89-95 (2010).
- [20] R.B. Perez-Saez, V. Recarte, M.L. Nó, J. San Juan, Anelastic contributions and transformed volume fraction during thermoelastic martensitic transformations, *Phys. Rev. B* **57**, 5684-5692 (1998).
- [21] R.B. Perez-Saez, V. Recarte, M.L. Nó, J. San Juan, Analysis of the internal friction spectra during martensitic transformation by a new temperature rate method, *J. Alloys Comp.* **310**, 334-338 (2000).
- [22] J. San Juan, R.B. Perez-Saez, Transitory effects, *Mat. Sci. Forum* **366-368**, 416-436 (2001).
- [23] J. Van Humbeeck, The martensitic transformation, *Mat. Sci. Forum* **366-368**, 382-415 (2001).
- [24] L. Dirand, M.L. Nó, K. Chastaing, A. Denquin, J. San Juan, Internal friction and dynamic modulus in Ru-50Nb ultra-high temperature shape memory alloys, *Appl. Phys. Lett.* **101**, 161909 (2012).
- [25] G. Gremaud, J.E. Bidaux, W. Benoit, Low-frequency study of internal friction peaks associated with a 1st-order phase transition, *Helv. Phys. Acta* **60**, 947-958 (1987).
- [26] M.L. Nó, L. Dirand, A. Denquin, L. Usategui, G.A. Lopez, J. San Juan, Internal friction during martensitic transformation in ultra-high temperature Ru-Nb shape memory alloys, *Mat. Today: Proc.* **2S3** (2015) S809-S812.
- [27] J. San Juan, L. Dirand, A. Denquin, G.A. Lopez, M.L. Nó, Martensite interfaces mobility and diffusion processes in Ru-Nb shape memory alloys studied by mechanical spectroscopy (to be published).