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EFFECT OF SURFACE MODIFICATION OF α-Ti ON INTERNAL FRICTION

ABSTRACT

The measurements of the internal friction were done using the RAK -3 relaxator at the bending mode oscillation of the acoustic frequency. The annealed α -Ti and α -Ti with the surface modified by the pulse mechanical grinding, by the plasma assisted formation of the layer of Ti-Al intermetallics and by the electrochemical hydrogen charging have been studied. The Young modulus and the attenuation of samples were measured at the heating of specimens between 200 and 600 K. In the studied temperature range, some relaxation processes occurred in the modified specimens. The values of the Young modulus and of the internal friction background have been also found to depend on the state of the Ti surface. The possible effects of the phase composition and the stress state on the obtained results have been discussed.

Key words: internal friction, resonance frequency, relaxation processes, surface modification, Ti-Al intermetallics, hydride

INTRODUCTION

In order to increase the hardness and the resistance to corrosion and wear, Ti and its alloys have been subjected to various surface treatments. The very important goal is to achieve the good adhesion of modified surface layer to the substrate, which might be attained if the substrate material participates in the formation of the surface layer.

In the mechanical pulse treatment [1] the energy of the friction at high speed has been used to modify the surface. In the tribological contact of the special tool and the treated part, the heating of the metal surface (at heat rate $0.05-2.0*10^6$ °C /s) with the simultaneous plastic deformation and the very quick cooling (at cooling rate $1-10*10^6$ °C /s) take place. The temperature within the contact may be $900 - 1000^0$ C for about (6-10)*10⁻² s. Using the appropriate cooling agents allows to achieve the high speed of cooling as well as to introduce some alloying element into the treated surface. As a result, the surface of increased hardness, nanosize grains and alloyed with C, N or Si has been formed [2].

The other possibility to obtain the surface layer of good adhesion is the deposition of Al on Ti and then the plasma treatment of obtained system [3]. As a result, the layer (3 to 20 μ m thick) consisting of the intermetallics of the Ti-Al system has been formed. Depending on the applied parameters, the phase composition of layer varies

and the phases being the result of reaction of Al with Ti and with residual gases are formed (including the nanolayer of Al_2O_3) causing the increase in the hardness, resistance to wear, corrosion and hydrogen absorption [4, 5].

At electrochemical hydrogen charging of α -Ti, hydrogen has been mostly concentrated within the surface layer, about 10 to 50 µm thick [6]. The formation of the supersaturated solid solution, the precipitation of hydride phase [7, 8, 9] and thus, the high deformation of α -Ti take place and substantially change the strength, the resistivity to corrosion and wear of the surface layer.

In the case of described above modifications of the thin surface layers, the evaluation of their elastic and plastic properties by the routine methods is quite ambiguous and complicated. Even measurements of microhardness may have great scattering depending on the layer thickness and the substrate properties. In this case, the valuable information on the elastic and anelastic properties of the surface layer may provide the internal friction measurements [10]. In those measurements done on the torsion or bending straining mode, the properties have been sampled from the thin surface layer. Internal friction measured vs. the oscillation frequency at constant temperature or vs. the temperature at constant frequency (mechanical spectroscopy) provides also the information concerning the phase composition and the state of the structural defects [10]. The formation of the internal friction peaks seen on the internal friction spectra reveals that some relaxation process in the metal structure has been activated at temperature of the peak by the application of oscillation. The appearance of the peak is supported by the step or change of the slope of the modulus vs. temperature relationship [10].

The aim of present work was to establish the effect of the differently modified surface layer of α -Ti on the layer elastic and anelastic properties as measured by the internal friction.

MATERIALS AND EXPERIMENTAL PROCEEDURE

Specimens (1 mm thick, 30 mm long and 10 mm wide) of annealed α -Ti (99.99%) and of the two-phase ($\alpha + \beta$) Ti-6Al-4V alloy were used. One surface of α -Ti specimens was subjected to the surface modification by mechanical pulse treatment (MP), by plasma assisted formation of Ti-Al intermetallic layer (PA) method and by hydrogen charging (HC). The MP treatment was done at the tool pressure 600 N and linear velocity 70m/s. The cooling media were [2]: 1) mineral oil with the addition of low-molecular polyethylene for carburization of surface layer (sample code Ti-C) and 2) the 10% solution of aminile for nitriding of surface layer (sample code Ti-N). In the PA treatment, Al was deposited on α -Ti surface by magnetron sputtering and the samples were then subjected to the glow discharge in Ar, at 560^o C (sample code (Ti-Al)/Ti). The hydrogen charging was done electrochemically at cathodic polarization (5 and 830 mA/cm²) in 0.1 M NaOH solution for up to 60 min (sample code Ti-5H and Ti-830H). The thickness of the modified layer was about 10 to 50 µm.

The internal friction and the resonance frequency were measured at the bending strain mode using the resonance mechanical spectrometer RAK-3 equipped with the vacuum chamber and the cooling and heating facility controlled by the computer [11]. The specimen was mounted as a beam between two electrodes as schematically shown

in Figure 1. The sinusoidal voltage was applied to excite the bending oscillation of acoustic frequency. The amplitude independent measurements were done at the strain amplitude $\varepsilon = 1 \times 10^{-4}$ at heating from 180 K to 600 K with a heating rate 3 K/min. The procedure was repeated 2 times. From the obtained results, the values of internal friction (Q⁻¹) and of the dynamic Young modulus (E) have been calculated according to the equations (1) and (2) [10, 11], respectively.

$$Q^{-1} = \frac{1}{\pi} \ln \frac{A_N}{A_{N+1}}$$
(1)

where: A_N and A_{N+1} – the consequent values of amplitude of oscillation.

$$E = 94,68 \left(\frac{l_r}{h}\right)^3 \cdot \frac{m_d}{b} \cdot f^2$$
(2)

where: l_r , h, b and m_d –length, thickness, width and mass of the vibrating part of the sample, respectively; f – the automatically measured resonance frequency.



Fig. 1. Schematic presentation of the bending mode oscillation of studied samples for the internal friction and elastic modulus measurements

The evaluated change of the elastic modulus and of the internal friction vs. temperature (internal friction spectra) obtained for specimens with modified surface have been compared with those obtained for pure Ti.

RESULTS AND DISCUSSION

The change of elastic modulus of studied materials in comparison to that in α -Ti (E_{alloy}/E_{Ti}) and the values of internal friction background (Q⁻¹) as measured for studied materials at temperature (T_b) corresponding to the part of mechanical spectra where no relaxation process occurs are presented in Table 1.The temperature and the height of the internal friction peaks occurred in the internal friction of studied materials is collected in Table 2.

material	T _b [K]	E _{alloy} /E _{Ti} at T	$Q^{-}, 1x10^{-4}$
Ti	275	1	8
Ti-Al-V	275	0.585	8
(TiAl)/Ti	340	0.898	1.5
Ti-N	375	1.03	1
Ti-C	375	0.787	8
Ti-H, 5 mA/cm ²	200	0.210	500
Ti-H, 830 mA/cm ²	200	0.724	50

Table 1. Change of elastic modulus of studied materials in comparison to that in α -Ti (E_{alloy}/E_{Ti}) and internal friction background (Q^{-1}) as measured for studied materials at temperature (T_b) at which no peaks appear in spectra

Table 2. Temperature and height of the internal friction peaks appeared in internal friction spectra of studied materials

matarial	Haating	D	Ω^{-1} v 10 ⁻⁴	D	Ω^{-1} v 10 ⁻⁴
material	пеацій	\mathbf{r}_1	Q XIU	P_2	Q XIU
		[K]		[K]	
Ti	Ι	no	-	no	-
Ti-Al-V	Ι	200	8	500	130
	II	310	8	525	70
(TiAl)/Ti	Ι	250	1	440	38
	II	250	1	465	42
Ti-N	Ι	220	13	no	
	II	245	9		
Ti-C	Ι	320	18	no	no
	II	no	-	-	-
Ti-H, 5	Ι	300	20	575	750
mA/cm ²					
Ti-H, 830		no	-	no	-
mA/cm ²					

Fig. 2 presents the typical mechanical spectra and temperature dependencies of elastic modulus for untreated materials. In the case of pure Ti (Fig. 2a) no internal friction peak revealing the relaxation process occurs within the studied temperature range. The elastic modulus monotonously decreases with the increased temperature.

In the case of the two-phase $(\alpha + \beta)$ alloy Ti-Al-V alloy, the distinct internal friction peak appears at about 500 K on the spectra recorded at first heating, associated with the change of the slop of the elastic modulus relationship (Fig. 2b). Comparison of results for the $(\alpha + \beta)$ alloy (Fig. 2a) and for α -Ti (Fig. 2b) may suggest the peak to be associated with the presence of the second phase. In the case of multiphase material, the origin of the peak may be [10, 12]: 1) the relaxation processes within the second phase, 2) the phase transformation taken place at the peak temperature and 3) the dislocation processes. Indeed, the β - Ti $\leftrightarrow \alpha$ – Ti transformation with the decomposition of β - phase may occur at the peak temperature (according to [7]) and cause the peak formation. On the other hand, the presence of the second phase increases the dislocation density in the base phase and thus, the observed peak may be associated with the dislocation.



Fig. 2. Examples of typical temperature relationships of elastic modulus (E) and internal friction (Q⁻¹) obtained for studied materials: (a) – Ti; (b) – Ti-Al-V alloy

As seen in Fig. 2b and Table 2, at the second heating the peak decreases and shifts to the higher temperature, in comparison with the first one. However, the level of the internal friction background being responsible for the dislocation movement does not change (Table 1). Therefore, the formation of the peak should be associated not with the dislocation processes but rather with the processes occurred in the β phase, amount of which decreases due to the transformation into the α - phase during the first heating. Such a transformation has been shown in [7]. As follows from Table 1, the elastic modulus of the alloy is much lower, but the internal friction background is quite similar to the appropriate values obtained for pure Ti.



Fig. 3. Temperature relationships of elastic modulus (E) and internal friction (Q⁻¹) obtained for Ti with the modified surface by MP treatment (Ti-C and Ti-N specimens)

Fig. 3 presents the internal friction spectra for the specimens subjected to the mechanical pulse treatment. In both cases the spectra reveal the internal friction peaks, temperature and height of which are shown in Table 2. In the case of Ti-C material the broad peak not having the Debay shape disappears at the second heating of specimen (Fig. 3). Therefore, the peak is supposedly associated with some instability of the structure of modified surface as supported the change of the elastic modulus due to the heating. However, even after heating, the internal friction background remains much higher and the elastic modulus lower than those values obtained for pure Ti (Fig. 3).

In the case of Ti-N material, neither the peak nor the modulus have been substantially affected by the heating (Fig. 3). The Debay shape of the peak may suggest some relaxation process, probably associated with the formation of new phase (TiN) during the treatment [2]. In the case of Ti-N material the internal friction background was similar but the elastic modulus was slightly higher than the appropriate values obtained for pure Ti (Table 1).



Fig. 4. Temperature relationships of elastic modulus (E) and internal friction (Q⁻¹) obtained for (Ti-Al)/Ti specimens with the surface modified by the PA treatment

The internal friction spectra for (Ti-Al)/Ti material exhibit two distinct peaks of the Debay shape: P_1 and P_2 , cf. Fig. 4. At the second heating the height and the position of peak P_1 practically does not change, whereas P_2 peak shifts to the higher temperature without substantial change of the height. Some similarity might be traced between the behavior of the high temperature peak (P_1) seen in the spectra obtained for the (Ti-Al)/Ti and for the Ti-Al-V (Fig. 2b) materials, suggesting the similar relaxation processes occurring in both cases. On the other hand, the low temperature peak P_2 is quite similar to one observed for the Ti-N material (Table 2, Fig. 3). It should be noted that despite the plasma treatment was done in Ar, the formation of TiN and TiAlN phases have been detected [4, 5] within the modified layer. Taking onto account the presence of the nitride phase and the appearance of the quite similar peaks in Ti-N and in (Ti-Al)/Ti materials, this peak may be accounted for the relaxation associated with the nitride. The values of the elastic modulus and of the background of (Ti-Al)/Ti material are slightly lower than those parameters recorded for pure Ti (Table 1).

Fig. 5 presents the spectra for hydrogen charged specimens. At low polarization two peaks are observed: the very distinct high temperature peak P_2 and the much lower

low temperature peak P_I , temperature and heath of which are shown in Table 2. The relaxation mode of the peaks has been supported by the change of the slop of modulus vs. temperature. It should be noted that elastic modulus of the material hydrogen charged at low polarization is distinctly lower whereas the materials internal friction background is much higher than the appropriate values measured for pure Ti (Table 1).

In the literature, the various relaxation processes have been accounted for the formation of the 250-300 K internal friction peaks detected at acoustic frequency in hydrogen charged Ti and its alloys. The following processes have been considered by different Authors:

- The reaction of the hydride ↔ dissolved hydrogen in α-Ti matrix [13, 14] consisting of the dissolution of hydride particles to produce the stress field in the matrix which in turn causes the lattice parameters to undergo a quasi viscous change (the Koster relaxation) [13];
- The interaction of hydrogen di-interstitials in α-Ti solid solution with dislocation loops (the Hasiguti model) [15];
- The stress-induced change of the atomic order which involves the diffusion jumps of atoms (Zener relaxation) [16].



Fig. 5. Temperature relationships of elastic modulus (E) and internal friction (Q⁻¹) obtained for Ti-H specimens with the surface modified by hydrogen charging treatment at different cathodic polarization

It should be also emphasized that although in [13 and 14] the 250 K peak has been accounted to the hydride formation, in [17] the peak occurred at 600 K has been considered as the hydride transformation strain-induced peak in the hydrogen charged Ti and Nb-Ti alloys. Taking into account such a great difference in the explanation of the nature of the hydrogen internal friction peaks in Ti, it is difficult to judge the origin of the peaks observed in the studied case, moreover than the material state is very complex. As has been described in [18] the application of the low cathodic polarization causes the dissolution of hydrogen in the metal lattice and the precipitation of the hydride phase. Those processes are associated with formation of stresses, which might be confirmed by the observed in the present the very high internal friction background (Table 2) suggesting the increase in the density of vibrating dislocations [10] due to the hydrogen charging.

It should be emphasized that the hydrogen charging at the low cathodic polarization causes the distinct decrease in the elastic modulus, which suggests the intrinsic softening of the α – Ti due to the hydrogen charging under the above conditions.

The material charged with hydrogen at application of the high cathodic polarization reveals no internal friction peaks to occur within the studied temperature region (Fig. 5). However, the elastic modulus is slightly lower and the internal friction background higher than the corresponding values observed in the case of Ti, cf. Table 1.

Although the exact nature of the internal friction peaks observed in the PM and PA surface treated materials cannot be exactly explained, the obtained internal friction spectra will serve as those described the material initial state an will be compared with the obtained at the application of the hydrogen charging in the future work.

CONCLUSIONS

- 1. The internal friction measurements done in the bending mode at application the acoustic frequency is a good tool to study the changes in the elastic and anelastic properties within the surface layer, $10 30 \mu m$ thick, caused by the surface treatment of Ti.
- 2. Within the studied temperature range (200 to 600 K) the internal friction peaks not occurred in the pure Ti have been detected in the differently surface treated materials.
- 3. The internal friction spectra of the electrochemically hydrogen charged Ti distinctly differ, depending on the value of cathodic polarization. Two internal friction peaks have been observed in the material hydrogen charged at the low cathodic polarization and no peaks reveals material charged at the high cathodic polarization.
- 4. The hydrogen charging of α -Ti with the low cathodic polarization causes the distinct decrease in the Young elastic modulus revealing the material softening.

ACKNOWLEDGEMENT

The present study has been has been carried out at the financial support provided by the grant 3T08C02630.

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