第 39 卷 第 11 期 金属学报 Vol.39 No.11
2003 年 11 月 1228—1232 页 ACTA METALLURGICA SINICA Nov. 2003 pp.1228–1232

EVALUATION OF THE SHEAR MODULUS OF THIN FILMS AND DETECTION OF THIN–OIL FILMS BY LOW–FREQUENCY MECHANICAL SPECTROSCOPY

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Supported by Polish State Committee for Scientific Research (KBN) (No.11.11.110.499), Volkswagen Stiftung (No.I/77 192) and National Natural Science Foundation of China (No.10274086)
Manuscript received 2003–07–09

ABSTRACT The basic concept for the low–frequency mechanical spectrometer operating both in the resonant and subresonant mode is described. Two methods for studying the physical properties of thin films on a metallic substrate are briefly presented. The first method makes possible measurements of the shear modulus and internal friction of a TiN/Ti(C, N) multi–layer film deposited on a Mo wire. The second method enables detection of extremely fine traces of oil film present on the surface of steel sheets. Although the two techniques described in this paper have different applications, they are both related to surface effects which result in loss of mechanical energy.
KEY WORDS internal friction, mechanical spectroscopy, shear modulus, thin film, oil film

低频机械谱术测量薄膜切变模量及微量油膜探测 *

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摘 要 描述了工作在共振和次共振模式下的低频机械波谱仪的基本原理. 主要介绍了研究金属衬底上薄膜的物理性质的两种方法: 第一种方法, 用于测量沉积在钼丝上的 TiN/Ti(C, N) 多层膜的切变模量和内耗; 第二种方法, 用于探测钢片表面微量油膜的存在. 尽管这两种技术有着各自不同的应用目的及对象, 但它们均源自能够导致机械能损耗的表面效应.

关键词 内耗, 机械波谱学, 切变模量, 薄膜, 油膜
中图法分类号 TG113.22 **文献标识码** A **文章编号** 0412–1961(2003)11–1228–05

1 Introduction

Low–frequency mechanical spectrometers are used to study loss of mechanical energy (internal friction or mechanical loss angle) and the shear modulus of bulk specimens. It is noteworthy that low–frequency mechanical spectroscopy can also be successfully used to study thin films deposited on a substrate. The success of this particular application is twofold: (1) it enables direct measurements of the shear modulus of a thin film deposited on the metallic substrate and (2) it allows detection of a thin–oil film present on the metallic substrate due to the appearance of characteristic low temperature mechanical loss peaks.

Although measurements of the shear modulus of thin films were attempted using a wide range of different techniques closely related to mechanical spectroscopy [1], here we confine our interest to low–frequency mechanical spectroscopy. In the following sections we shall provide the formulas for evaluating the shear modulus and internal friction of a thin film deposited on a cylindrical substrate. An exam-

* 波兰国家科学研究委员会基金 11.11.110.499, 大众汽车基金 I/77 192 和中国国家自然科学基金 10274086 资助项目
收稿日期: 2003–07–09
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ple will be given of a TiN/Ti(C, N) multi–layer thin film deposited on a Mo wire studied in a standard torsion pendulum operating in the resonant mode around 1 Hz.

Fine traces of rolling oil left on the surface of cold–rolled steel sheets are usually undetectable using many experimental techniques. A large number of experimental attempts to detect extremely small traces of rolling oils on a steel substrate have not proved practical or reliable. It has been shown that the presence of a thin film of rolling oil on metallic substrate unequivocally yields characteristic low temperature internal friction spectra. Hence, it is demonstrated that low–frequency resonant and/or subresonant mechanical spectroscopy can be successfully used to detect and to study the physical properties of oil films on metallic substrates.

2 Concept for a low–frequency mechanical spectrometer designed to operate in the subresonant and resonant mode

The schematic diagram of a low–frequency mechanical spectrometer operating both in the resonant (free decaying oscillations) and subresonant (forced oscillations) mode is shown in Fig.1 [2].

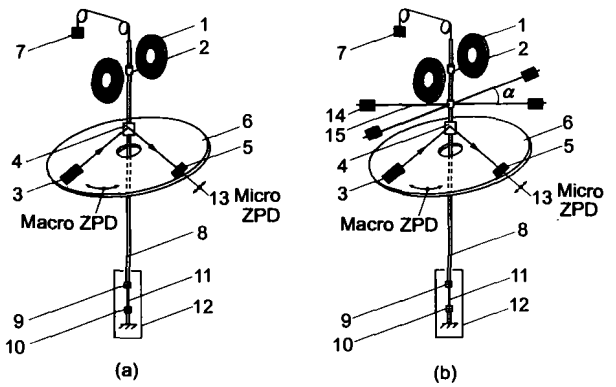

Fig.1 Schematic illustration of a multifunctional mechanical spectrometer (1—Excitation coils, 2—Magnet, 3—Diode laser, 4—Aluminum or silver coated thin mirror, 5—Photo–detector, 6—Movable support, which allows the rotation of the entire upper part of the spectrometer by a computer–controlled step–motor attachment to correct for macro ZPD (zero–point drift), 7—Counterweight, 8—Inertia member, 9—Upper grip, 10—Lower grip with a movable base, 11—Sample, 12—Furnace, 13—Micro ZPD is separately controlled by a computer–controlled step–motor attachment[2], 14—Weight, 15—Arm; α=90°)
(a) subresonant mode (b) resonant mode

In the resonant mode, the system determines the loss of mechanical energy by measuring the logarithmic decrement δ of free decaying oscillations during a user–determined temperature ramp sequence. The optimization strategy for measurements of the logarithmic decrement comprises: (1) a selection of optimal computing algorithms used for calculating δ, (2) a selection of signal acquisition parameters (*e.g.* the sampling frequency, the length of the free decaying signal used for signal acquisition, s ignal–to–noise ratio S/N, *etc*), and (3) signal analysis method. Measurement techniques and numerical algorithms used to calculate the logarithmic decrement were recently reviewed by Magalas *et al* [3].

In the subresonant mode, the system determines mechanical loss in isothermal conditions by measuring the mechanical loss angle φ between the purely harmonic applied stress signal (steady–state time–harmonic signal) and the resulting strain response signal. Frequency sweeps are usually carried out in a frequency range between around 10 Hz and 10^{-4} Hz. The mechanical loss angle φ is calculated on the basis of the phase difference between the stress and strain response signals calculated using the Fourier transform or the Hilbert transform [4].

Modern mechanical spectrometers can accommodate samples of different geometrical form (*e.g.* wires or platelets), length, and stiffness [1,2,4]. The lower part of the sample is usually clamped onto a rigid grip fixed to the so–called 'base'. The upper part of the sample is fixed to an upper grip, which is attached to a rod (see Fig.1). Variation in a sample's length is possible in the mechanical spectrometer thanks to the special design of the lower part of the spectrometer, which allows vertical displacement of the 'base' of the lower grip (see part 10 in Fig. 1). The movable 'base' of the lower grip allows easy length variation in the sample from about 5 mm up to around 150 mm. The system can also operate with samples possessing drastically different levels of stiffness by changing the neodymium magnet (adjusting the mass and/or the shape of the magnet) which is affixed to the inertia member. This procedure is required to assure optimal signal acquisition strategy, which guarantees high accuracy in mechanical loss measurements [2–4].

The suspension section of the inertia member connects the inertia member to the suspension system via a pin–vise that holds a thin molybdenum wire that attaches to the suspension system counterweight

as illustrated in Fig.1. The molybdenum wire goes through two pulleys, so that only a negligibly small force is exerted on the sample to avoid any side effects such as (1) external bias stress and (2) the high temperature creep of the sample [1,2]. It is worth emphasizing that the basic concept underlying any modern low-frequency mechanical spectrometer is based on Ke's original design, well-known as the 'inverted torsion pendulum' or 'Ke's pendulum'.

The mechanical spectrometer is excited into torsional oscillations by an excitation system which consists of only a few parts: a digital frequency generator, an amplifier, the Helmholtz coil, and a magnet. The torque is applied to the system through the interaction between a pair of electromagnetic coils and a Nd-Fe-B magnet. The magnet is a hollow cylinder, with the inertia member running through its axis of rotation. The excitation system is designed so as to assure that the movement of the magnet takes place in a homogeneous electromagnetic field generated by the coils. In the subresonant mode the excitation signal is a pure sine signal with a pre-selected constant frequency generated by a digital frequency generator. In the resonant mode the excitation is done by an auto-control system to assure optimal time-length of steady-state oscillations with a constant amplitude of oscillations before free decay begins [2].

It is interesting to note that the mechanical spectrometer is equipped with two computer-controlled step-motors for an automatic correction of zero-point drift (ZPD) [2]. A macro displacement of the upper part of the spectrometer allows easy automatic centering of the system while micro ZPD correction allows fine adjustment of the photo-detector. The micro ZPD system operates only in the time intervals between measurements of two successive experimental points. The role and influence of the ZPD on computations of the logarithmic decrement in bulk specimens will be described elsewhere.

The angular displacement of the inertia member of the spectrometer is measured using a laser that reflects on a mirror attached to the inertia member and is received by a photo-detector. The detector provides a high-quality strain response signal (S/N=100/1).

The quality of the strain response signal recorded in a mechanical spectrometer is analyzed using the 'signal quality test'. This test comprises the standard FFT (fast Fourier transform) and the wavelet transform of the strain response signal, which yields a three-dimensional representation of the signal: time, frequency, and amplitude [4,5]. The 'signal quality test' enables detection of any undesirable frequency components in the strain response signal and variation in the frequency components of the strain response signal over time. We recall that the purpose of performing the 'signal quality test' based on the wavelet transform is to obtain time and frequency information regarding the strain response signal simultaneously [2-4,6]. The time-frequency joint representation of the strain response signal is called the 'identified strain response signal (ISRS)'[4]. The use of the 'signal quality test' and the ISRS is frequently crucial and particularly useful after readjustments are made to the mechanical parts of the spectrometer and after installation of a new sample possessing the following features: (1) an imperfect geometry, (2) it is too long or (3) it has too small a radius or in general very little thickness.

3 Evaluation of the shear modulus and internal friction of a multi-layer film deposited on a Mo substrate

As shown by Li and Fang *et al.*[1] the shear modulus G and internal friction Q^{-1} of the film (f) deposited on the metallic substrate (s) can be readily obtained by measuring the internal friction and the resonance frequency of the torsion pendulum with the bare substrate and with the composite sample (c). The shear modulus of the TiN/Ti(N, C) multi-layer film G_f deposited on a Mo wire is given by [1]

$$G_f = \frac{\Phi - 1}{(1+\delta)^4 - 1} G_s$$

where $\delta = d_f/R_s$ and d_f denotes the thickness of the film and R_s is the radius of the specimen. The Φ parameter is given by

$$\Phi = (f_c^2 l_c)/(f_s^2 l_s)$$

where f_c and l_c denote the resonance frequency and the length of the composite sample while f_s and l_s denote the resonance frequency and the length of the substrate. A typical example of the shear modulus and the internal friction of the TiN/Ti(N, C) multi-layer film deposited on a Mo wire deduced from mechanical loss measurements of the bare substrate and the composite sample is illustrated in Fig.2.

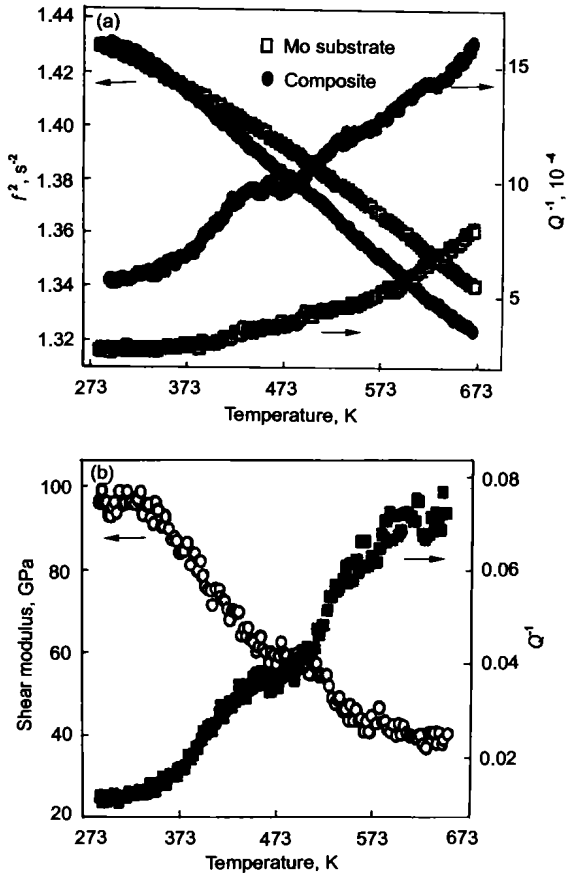

Fig.2 The internal friction and the shear modulus (proportional to the square of the resonant frequency, $G \propto f^2$) for the Mo substrate and for the composite sample (a), and the TiN/Ti(N, C) multi-layer film (b) as deduced from Fig.2a by Li and Fang *et al.*[1]

As intimated by Li and Fang *et al.*[1] the internal friction Q_c^{-1}, Q_s^{-1} and the resonant frequencies f_c and f_s can be measured with sufficient accuracy. It is recommended, however, that several measurements be made with different sample lengths and the infinite sample length extrapolated [6] in order to avoid uncertainties regarding the valid sample length due to clamping. The moveable 'base' of the lower grip referred to earlier makes possible the above mentioned experimental procedure. Another source of error in determining the shear modulus is caused by imprecise measurements of the thickness of the film. This effect does not affect measurements of internal friction.

4 Detection of the presence of extremely fine oil layer on a steel substrate

Fig.3 shows a typical example of internal friction observed in a composite sample, *i.e.*, the metallic substrate (a commercial ferrite steel sheet) covered with

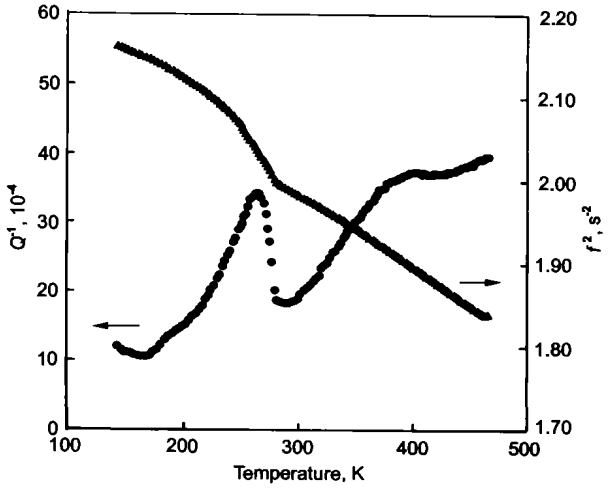

Fig.3 A typical example of internal friction and shear modulus induced by the presence of oil film containing 0.7%S deposited on a steel substrate, the peak at around 270 K and the corresponding variation of the shear modulus to be caused by the glass transition of the oil and the high temperature peak to be the SK peak caused by the substrate

a thin film of rolling oil [7–9]. The low-temperature peak at around 270 K is entirely caused by the surface effect, *i.e.*, by a glass transition of the oil [7,9]. The 270 K peak overlaps on the low-temperature side of the Snoek-Köster (SK) peak [10]. We recall that the SK peak is caused by dissipation of mechanical energy in the metallic substrate due to the interaction of dislocations with the Cottrell atmosphere of foreign interstitial atoms [10].

It is critically important to recognize that the 270 K peak is present even in cases where extremely fine traces of island-type oil films are present on the surface of the metallic substrate. The resonant and subresonant mechanical spectroscopy has already been successfully applied to detect rolling oils on the surface of cold-rolled steel sheets [7]. A typical example of the 270 K peak overlapping on the low-temperature side of the SK peak observed in a sample taken from an industrially cleaned steel sheet is shown in Fig.4. The presence of the 270 K peak enables detection of oil films not visible using a scanning electron microscope.

It can be concluded that low-frequency mechanical spectroscopy can be used to identify the degradation level of lubricant-oils caused by internal and external contamination due to hostile working conditions. This technique can be used for both mineral (petroleum-based) oils and synthetic (polyol ester-

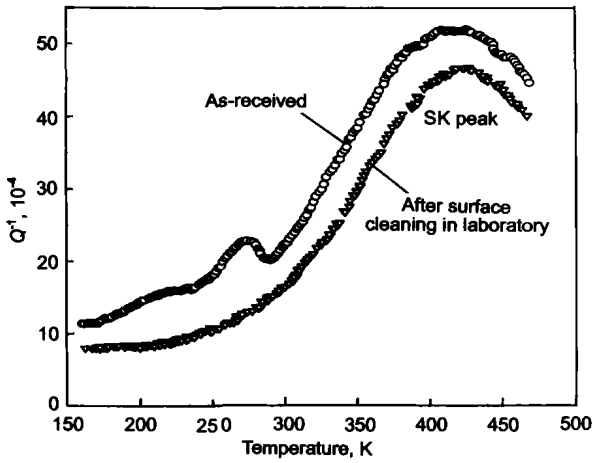

Fig.4 Effect of careful surface cleaning on the 270 K peak observed in steel sheets after industrial cleaning (as-received state) [7]

based) oils. Classical studies of oil films using infrared spectroscopy (FT-IR) can now be supplemented by mechanical loss measurements. A new application of mechanical spectroscopy is advocated for the petroleum and automotive industries. It is worth reiterating the fact as shown in this work and illustrated earlier by Li, Fang *et al.* [1] that a modern torsion pendulum can be used to study thin films of various origins [1,7–9]. A study of the time-evolution of the physical properties of oil films using mechanical spectroscopy is also feasible [7–9].

5 Conclusions

Mechanical spectroscopy can be successfully used to study thin films deposited on a metallic substrate. Although it is customary for mechanical spectroscopists to study bulk materials it has been demonstrated in this paper that mechanical spectroscopy is a sensitive tool for studying surface-related effects such as (1) the shear modulus of a thin film deposited on the metallic substrate and (2) the detection of oil films on the surface of steel sheets.

REFERENCES

[1] Li Z S, Fang Q F, Veprek S, Li S Z. *Rev Sci Instrum*, 2003; 74: 2477

[2] Magalas L B, Malinowski T. *Solid State Phenom*, 2003; 89: 349

[3] Magalas L B, Malinowski T. *Solid State Phenom*, 2003; 89: 247

[4] Magalas L B. *J Alloy Compd*, 2000; 310: 269

[5] Mencik J, Munz D, Quandt E, Ludwig A. *Z Metallkd*, 1999; 90: 766

[6] Magalas L B, Kwasniewski J. *Solid State Phenom*, 2003; 89: 355

[7] Magalas L B, Etienne S, David L, Malinowski T. *Solid State Phenom*, 2003; 89: 321

[8] Magalas L B, Malinowski T, Etienne S, David L, Kostro J. *Non-Destr Test*, 2000; 5: 223
(Warsaw: SIMP, Poland, 2000)

[9] Magalas L B, Etienne S, David L. *Non-Destr Test*, 2002; 7: 257
(Warsaw: SIMP, Poland, 2002)

[10] Magalas L B. *Acta Metall Sin*, 2003; 39: 1145
(Magalas L B. 金属学报, 20030; 39: 1145)