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THE INFLUENCE OF HYDROCARBON SURFACE LAYER ON THE INTERNAL FRICTION IN METAL SAMPLES

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Résumé. Nous avons étudié en fonction de la température la variation du frottement intérieur d'un composite constitué par un métal recouvert d'une couche d'hydrocarbure saturé. Le calcul de l'amortissement et du module de cisaillement de la couche a été réalisé à l'aide du modèle rhéologique de Maxwell. De plus nous avons obtenu la variation du temps de relaxation.

Abstract - The internal friction of metal and alloy samples covered with a thin layer of saturated hydrocarbon was measured using the torsion pendulum technique. An attempt was made to separate the internal friction and shear modulus of surface layer. The Maxwell rheological model of a layer was used for the description of experimental results. The temperature dependence of relaxation time was obtained.

EXPERIMENTAL PROCEDURE

The measurements of internal friction were performed with a torsion pendulum oscillating at 0.5 to 3.5 Hz and in the temperature range 150 to 300 K. The samples made from Au, Pt, Cu, Mo as well as from CoPt and Fe+0.2%Ti alloys had a form of wire 1.0 to 1.5 mm in diameter and 60 to 70 mm in length. After mounting the samples in the pendulum they were preheated and the internal friction spectra of clean samples were recorded. Then the samples were covered with a layer of hydrocarbon $C_{10}H_{22}$, $C_{12}H_{26}$, $C_{14}H_{30}$, and $C_{16}H_{34}$. The thickness of hydrocarbon layer was estimated as about 2 μm . The logarithmic decrement of free vibrations damping δ was determined $/Q^{-1} = \delta/\pi/$. Simultaneously the frequency of vibrations f was recorded. The square of frequency is proportional to the shear modulus $/f^2 \sim G/$. The heating rate of the sample was about 1.5 K/min.

RESULTS AND DISCUSSION

In Table I there are listed the values of temperatures for internal friction peak for CoPt samples covered with different hydrocarbon layers as well as melting temperatures for these hydrocarbons [1]. Good agreement between the peak temperature T_M and melting

temperature of hydrocarbon confirms the hypothesis that the internal friction peak appears at the melting temperature of the surface layer. Fig. 1 shows the typical internal friction spectra $Q^{-1}/T/$ and shear modulus changes $f^2/T/$ for Cu, Au and Fe+0.2%Ti samples covered with $C_{16}H_{34}$ hydrocarbon. Similar dependences were found for all tested samples. An asymmetric character of the peak is clearly seen as well as the regular changes of vibration frequency for the samples with hydrocarbon layer. For the temperatures higher than T_M the vibration frequency of covered samples reaches the values characteristic for uncoated sample.

The shape of the high temperature slope of the peak is approximated because of the deformation peak which appears on the covered sample [2]. Fig. 2 shows the dependence between the maximum heights ΔQ_M^{-1} and the shear modulus defect $\Delta G/G$. The modulus defect due to hydrocarbon layer was obtained as $(f_0^2 - f_B^2)/f_B^2$ at 220 K/ where f_0 and f_B are vibration frequencies for coated and uncoated sample, respectively.

Table I

CoPt sample with hydrocarbon layer	temperature of $Q^{-1}/T/$ maximum	melting temperature [1]	
		experim.	theoret.
$C_{10}H_{22}$	~ 230 K	242 K	230 K
$C_{12}H_{26}$	~ 260 K	250 K	263 K
$C_{14}H_{30}$	~ 275 K	278 K	270 K
$C_{16}H_{34}$	~ 290 K	293 K	286 K

The linear dependence between ΔQ_M^{-1} and $\Delta G/G$ may suggests that in the case of different materials covered with the same hydrocarbon there is the same mechanism responsible for the formation of internal friction peak. In Fig. 2 there are also included the data obtained from annealing measurements of hydrocarbon layer.

Basing on Lefevre [3] and Shermiorgor [4] models an attempt was made to calculate the internal friction and shear modulus for hydrocarbon surface layer. Neglecting the effects connected with interactions between hydrocarbon layer and the bulk and assuming that:

- the layer in a form of cylinder is rigidly bonded to the substrat,
- elastic energy W_0 stored in the sample is the sum of energy stored in the layer W_L and in the bulk W_B ,
- energy dissipated in one period of stress changes W_0 is the sum of energies dissipated in the layer and in the bulk,

we obtained the following relations for

a/ internal friction in surface layer:

$$Q_L^{-1} = \left\{ Q_0^{-1} - Q_B^{-1} \left(\frac{f_B}{f_0} \right)^2 \right\} : \left\{ 1 - \left(\frac{f_B}{f_0} \right)^2 \right\} \quad /1/$$

b/ shear modulus of surface layer:

$$G'_L = A (f_0^2 - f_B^2) : (R^4 - r^4) \quad /2/$$

where Q_0^{-1} , f_0 and Q_B^{-1} , f_B are the internal friction and vibration frequency for coated and uncoated sample, respectively; r is the radius of uncoated sample, $R = r + x$ is the radius of sample covered with a layer of thickness x . The constant $A = 8\pi \cdot I l$ /from the relation $f^2 = GR^4 / 8\pi I l$ / where l is the length of the sample and I is the moment of inertia of vibrating system.

The temperature dependence of internal friction for surface layer Q_L^{-1} obtained with eq. /1/ for Cu, Au and Fe+0.2%Ti samples covered with $C_{16}H_{34}$ hydrocarbon is shown in Fig. 3. The equation /1/ is very sensitive to f_0^2 changes as well as to Q_0^{-1} values. In the high temperature range the deformation peak makes impossible the precise determination of the main maximum slope. Because of this inaccuracy the calculations were performed down to T_M only. It is important to notice that the runs of each curve are different though they were obtained for the same hydrocarbon layer. Hence, it is reasonable to assume that the separated internal friction Q_L^{-1} is not only due to hydrocarbon but is connected with the properties of the bulk-layer interface.

In Fig. 3 there is also included the typical change of separated shear modulus G_L / for Au+ $C_{16}H_{34}$ sample/. The distinct changes of shear modulus from zero $/T > T_M/$ to the maximum value $/T < T_M/$ are seen. Below the temperature of about 220 K shear modulus reaches the constant value.

Such character of Q_L^{-1} damping can be explained when we consider the layer as the maxwellian body with a single relaxation process and the bulk as an ideal elastic body. Then the general expression for complex modulus has a form:

$$G_0^* = G_B \frac{r^4}{R^4} + \left(G_{L0} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i G_{L0} \frac{\omega \tau}{1 + \omega^2 \tau^2} \right) \cdot \left(1 - \frac{r^4}{R^4} \right) \quad /3/$$

and

$$\frac{\Delta G}{G} = \frac{G_{L\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} (1 - r^4/R^4)}{G_B r^4/R^4} = \frac{f_0^2 - f_B^2}{f_B^2} \quad /4/$$

- the internal friction is defined as

$$Q_0^{-1} = G''/G' = \{\omega \tau [1 + (\Delta G/G)^{-1}]\}^{-1} \quad /5/$$

where ω is the angular velocity, τ is the time characteristic for relaxation process and $G_{L\infty}$ is shear modulus of hydrocarbon layer measured for very high vibration frequencies.

Solving the eqns. /4/, /5/ the $Q_L^{-1} = 1/\omega \tau$ can be determined. The results are the same as presented in Fig. 3, as expected.

Obtained values of $\omega \tau$ allow to calculate the temperature dependence of relaxation time τ . Fig. 4 shows the dependences of $\ln \tau$ vs $10^3/T$ determined for the samples presented in Fig. 1.

If we assume the validity of Arrhenius law, the activation energy E comes to be temperature dependent and its value increases with increase of temperature. Such discrepancy between the $\ln \tau$ vs T^{-1} dependence and that expected for adopted model indicates that the interaction process between a layer and the bulk should be taken into account when any real physical model of damping is proposed. The applied Maxwell model gives satisfactory but only formal description of experimental results. The quantitative discussion of our calculations should be verified by the results of supplementary measurements of dynamic properties of hydrocarbon.

CONCLUSIONS

1. It was confirmed that the temperature position of internal friction maximum corresponds with the melting temperature of surface layer.
2. The linear dependence between $\Delta G/G$ and ΔQ_M^{-1} suggests the same mechanism responsible for internal friction peak in the case of different samples covered with the given surface layer.
3. Differences between separated Q_L^{-1} curves for the same hydrocarbon require the assumption that the internal friction is due also to the properties of bulk-layer interface.

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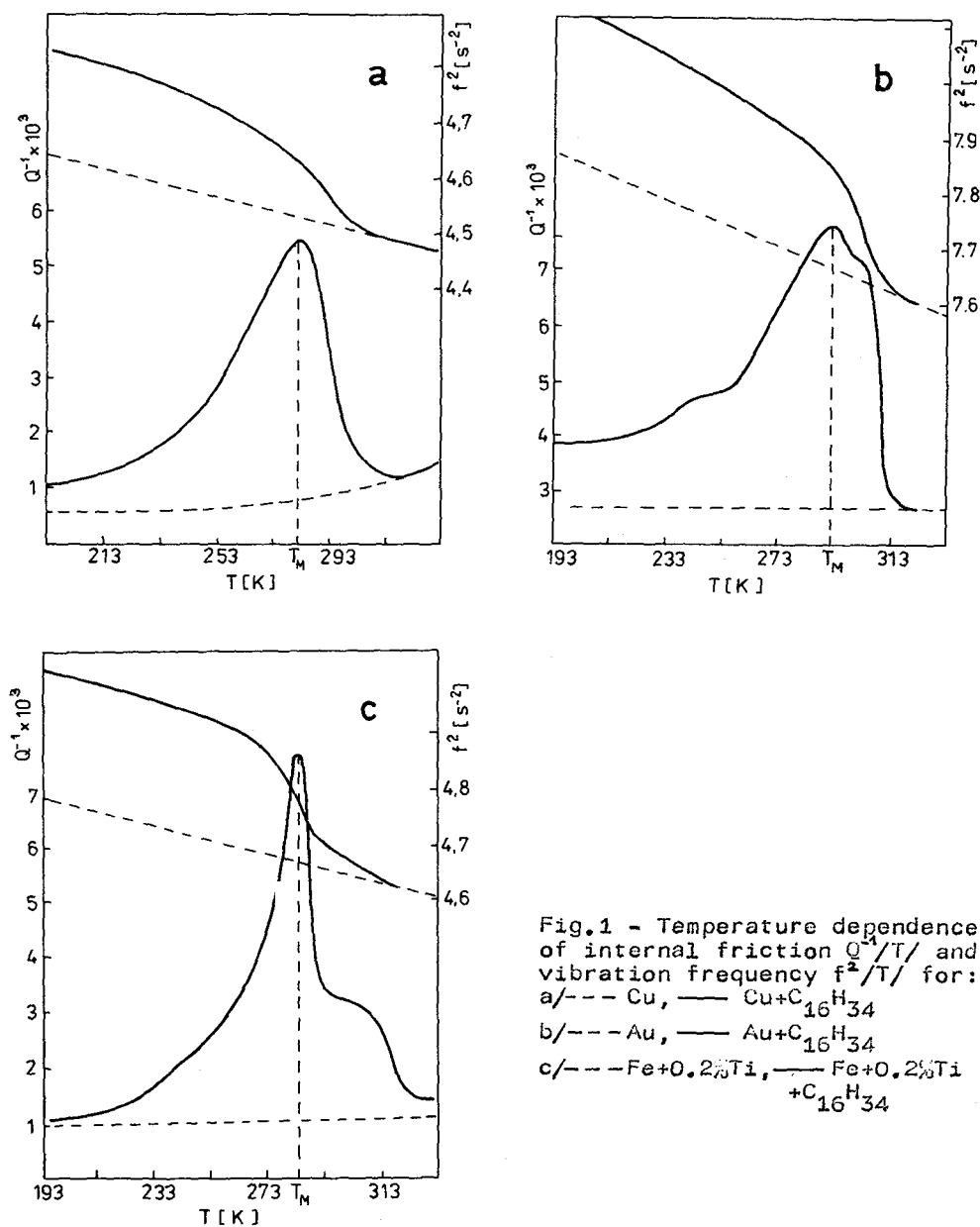


Fig.1 - Temperature dependence of internal friction Q^{-1}/T and vibration frequency f^2/T for:
 a/--- Cu, — Cu+C₁₆H₃₄
 b/--- Au, — Au+C₁₆H₃₄
 c/--- Fe+0.2%Ti, — Fe+0.2%Ti +C₁₆H₃₄

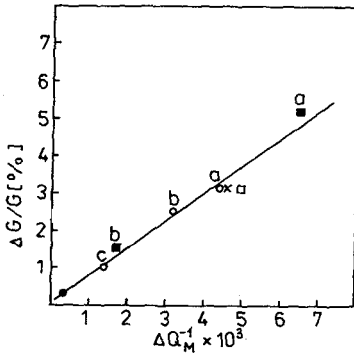


Fig. 2 - Dependence between ΔQ_M^{-1} and $\Delta G/G$ for:
 ○ - CoPt+C₁₆H₃₄ a/ nonannealed b/ annealed at 343 K
 c/ annealed at 363 K
 ■ - Fe+0.2Ti+C₁₆H₃₄ a/ nonannealed b/ annealed at 363 K
 □ - Au+C₁₆H₃₄, × - Cu+C₁₆H₃₄, ● - Mo+C₁₆H₃₄

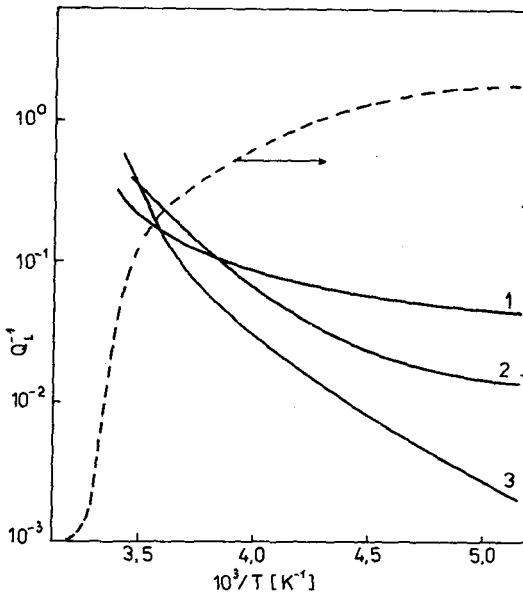


Fig. 3 - Temperature dependence of separated Q_L^{-1} for hydrocarbon layer determined from: 1/-Au, 2/-Cu, 3/-Fe+0.2Ti(+C₁₆H₃₄) measurements. Separated shear modulus G_L determined from Au+C₁₆H₃₄ measurement.

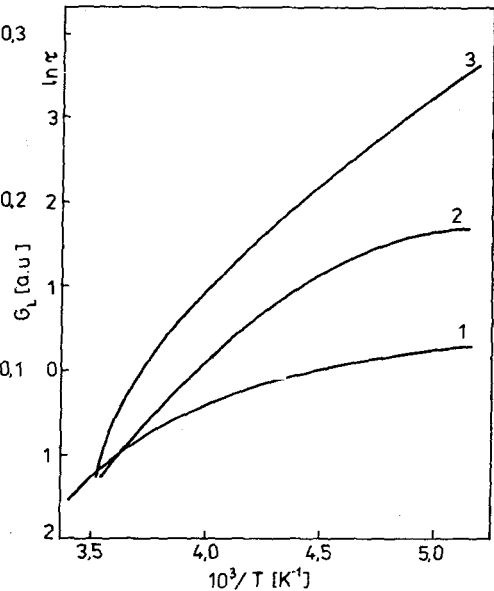


Fig. 4 - Temperature dependence of $\ln \zeta$ determined from: 1/-Au, 2/-Cu, 3/-Fe+0.2Ti(+C₁₆H₃₄) measurements.