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Influence of a changing microstructure on high temperature relaxation peaks, an example: WC–11wt.%Co

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Abstract

WC–11wt.%Co cemented carbide exhibits a relaxation peak at about 920 K in the 1 Hz frequency range. However, the values of the relaxation parameters are unusual. The apparent activation energy is higher than the self-diffusion energy and increases with the temperature from 3.5 eV to 7 eV. The apparent limiting relaxation rate of 10^{35} s^{-1} is much too high in comparison with a lattice vibration frequency. Moreover, superimposed on the relaxation peak, an extra damping is detected which is due to the heating or cooling rate ($\dot{T}$ effects). These phenomena can be interpreted as due to the evolution of the microstructure during the internal friction measurements. Effectively, taking into account the microstructural modifications, it is possible to modify the classical equation for dislocation damping in order to predict the shape of the associated relaxation peaks. Generalization of this approach can supply a method for analysing the damping peaks which present non-classical characteristics.

1. Introduction

The mechanical loss spectrum $Q^{-1}=Q^{-1}(\omega\tau)$ associated with the anelastic relaxation of a structural defect in a standard anelastic solid is described by [1]

$$Q^{-1}=\Delta\frac{\omega\tau}{1+\omega^2\tau^2} \tag{1}$$

where Δ and τ are the relaxation strength and relaxation time respectively, ω being the circular frequency. This equation is the well-known expression for a Debye peak, the maximum of which is obtained for

$$\omega\tau=1 \tag{2}$$

In the case of a thermally activated process, one assumes

$$\tau=\tau_0\exp(E/kT) \tag{3}$$

where E is the activation energy and k is Boltzmann's constant.

The peaks provide an Arrhenius plot and then

$$E=-k\frac{\mathrm{d}(\ln\omega)}{\mathrm{d}(1/T)}\quad\text{and}\quad\tau_0=\left(\frac{1}{\omega}\right)_{1/T=0} \tag{4}$$

In a stable microstructure, the values of E and τ_0 obtained in this way have a physical meaning. For instance, in the case of point defect relaxation, E is the diffusion energy and τ_0 the inverse of the Debye frequency (10^{13} Hz). However, if the above formalism is applied to the study of high temperature peaks, the obtained values for E and τ_0 are often not directly interpretable [2, 3]: E can be much greater than the self-diffusion energy and τ_0 can be of the order of 10^{-20}–10^{-40} s.

These values are apparent values obtained by the classical treatment of a damping spectrum which may be associated with a changing microstructure. The dependence of the microstructural state on the temperature has to be introduced in the above equations, where Δ, τ_0 and E are no longer constants but functions of the temperature: $\Delta=\Delta(T)$, $\tau_0=\tau_0(T)$ and $E=E(T)$. For instance, if $\Delta=\Delta(T)$ and the internal friction is measured in a classical way as a function of the temperature, the summit of the relaxation peak is not given by $\omega\tau=1$, but by the solution of

$$\frac{\mathrm{d}Q^{-1}}{\mathrm{d}(1/T)}=\frac{\mathrm{d}\Delta}{\mathrm{d}(1/T)}\frac{\omega\tau}{1+\omega^2\tau^2}+\Delta\frac{\mathrm{d}}{\mathrm{d}(1/T)}\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right)=0 \tag{5}$$

From this equation, it is possible to derive the relation between the circular frequency ω and the peak temperature T_P. The apparent activation energy is then given by the local slope of the curve $\ln(\omega)=f(1/T)$:

$$E_{\text{app}}=-k\left[\frac{\mathrm{d}(\ln\omega)}{\mathrm{d}(1/T)}\right]_{T=T_P} \tag{6}$$

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Equations (5) and (6) show that, in the case of a changing microstructure, one needs a microscopic model which specifies the functions $\Delta(T)$, $\tau_0(T)$ and $E(T)$ in order to analyse the mechanical loss spectrum more precisely. Results obtained in WC–Co hardmetal can serve as a good example.

2. Experimental results in WC–11wt.%Co

WC–11wt.%Co exhibits a rather simple mechanical loss spectrum at high temperature (Fig. 1), mainly composed of a relaxation peak (at about 920 K for a 1 Hz frequency) which is superimposed on an exponential increase in the background with the temperature [2, 4]. It has been proved that peak and high temperature background are due to energy dissipation mechanisms which take place in the cobalt binder phase [2, 4, 5]. The peak is a relaxation peak because it shifts in temperature when the frequency is modified. However, the activation energy (3.5–7 eV) determined from the temperature shift of the peak is higher than the self-diffusion energy in Co (2.7 eV) or than the diffusion energy of W in Co (2.5 eV). Also the limiting relaxation time $\tau_0 \approx 10^{-34}$ s is much too small to be associated directly with an attempt frequency. In addition, the activation energy determined by this method increases with the temperature (Fig. 2).

In addition, Fig. 3 shows that the level of damping depends on the heating or cooling rate $\dot{T}$. In Fig. 3, two curves have been plotted: one curve was measured during heating at a rate $\dot{T}$ of 0.03 K s^{-1} and the second in isothermal conditions. The difference between the two curves is due to transitory effects, called "$\dot{T}$ effects", which usually appear when the microstructure evolves with the temperature as for instance during phase transitions [6].

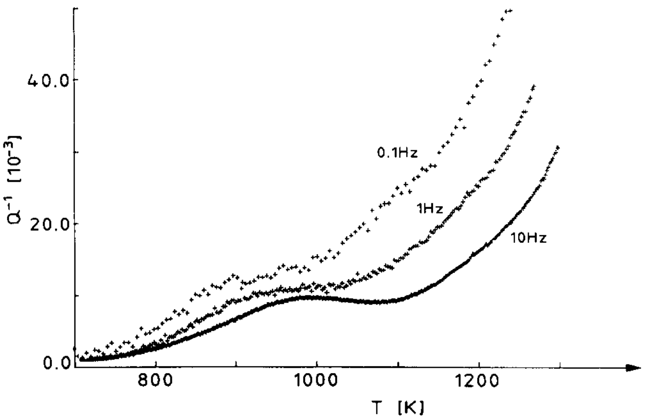

Fig. 1. Mechanical loss spectra of WC–11wt.%Co obtained in a forced pendulum during heating at a rate of 0.03 K s^{-1} (frequencies, 0.1 Hz, 1 Hz and 10 Hz).

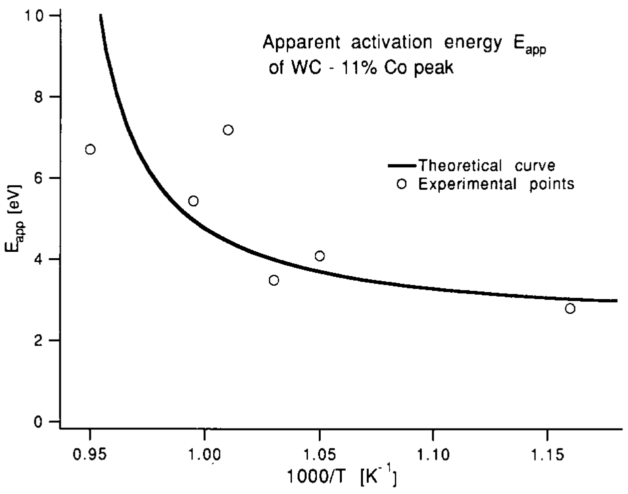

Fig. 2. Variation in the apparent activation energy E_{app} with the temperature: experimental points and theoretical curve deduced from our model.

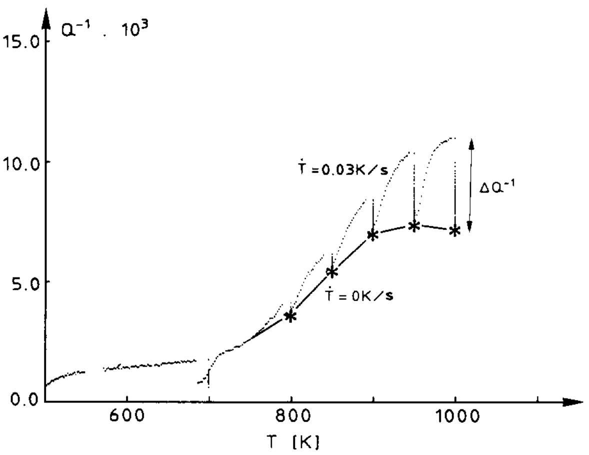

Fig. 3. Extra damping ΔQ^{-1} due to $\dot{T}$ effects and determined here as the difference between the curve obtained during heating at a rate of 0.03 K s^{-1} and isothermal measurements performed each 25 K after a waiting time of 30 min.

This phenomenon and the non-classical values of the thermodynamic parameters indicate that the relaxation process responsible for the peak in WC–Co takes place in a changing microstructure and consequently must be interpreted by a model which takes into account the evolution of the microstructure in the cobalt binder phase.

3. Model for the mechanical loss peak in WC–Co

The damping mechanism responsible for the internal friction peak in WC–Co takes place in the cobalt binder phase [2, 4, 5]. Transmission electron microscopy (TEM) observations of this phase have revealed that, at room temperature, the crystallographic structure of cobalt is f.c.c. with a large number of h.c.p. stacking faults strongly bound to each other [4]. All dislocations in the f.c.c.

phase are widely dissociated, the partials being trapped at the intersection between the slip planes (Lomer–Cottrell sessile dislocations). Damping at room temperature is weak, because the dislocations in the cobalt binder phase are pinned. If the temperature is increased above 700 K, one observes (*in situ* TEM experiments) a reduction in the stacking fault area caused by movement of the surrounding partial dislocations. As a consequence, the internal friction increases. In the temperature range of the peak, the microstructure of cobalt consists mainly of dislocation loops resulting from the recombination of the partials and which are pinned by more stable stacking faults. At higher temperature, more and more stacking faults disappear leading to an increase in the mobile dislocation density and in the dislocation loop length.

Let us assume that the high temperature internal friction of WC–Co is due to dislocation motion in the Co phase. The motion equation of a dislocation loop of length l is

$$B\dot{u}+Ku=\sigma b \tag{7}$$

where u is the mean displacement of the dislocation loop of length l, σb the applied force on the dislocation, $B\dot{u}$ the viscous dragging force and Ku the restoring force. Because the dislocations, which are responsible for the peak, are dissociated, the viscous force $B\dot{u}$, can be due to the dragging of tungsten (W) atoms which are trapped within the stacking faults between the partials (h.c.p. cobalt retains more W in solution than f.c.c. cobalt does). Then the viscous force coefficient B may be written as

$$B=c_W d\,\frac{kT}{D} \tag{8}$$

where c_W is the concentration of W in h.c.p. Co, D the diffusion coefficient of W in Co and d the distance between the two partials (extension of a stacking fault).

The distance d between the two partials is not constant. Effectively, *in situ* TEM experiments have shown that the stacking fault area decreases when temperature increases above 700 K. Let us write

$$d(T)=d_0\left(\frac{T_c-T}{T_c}\right)^2 \quad \text{for } T<T_c \tag{9}$$

where T_c is a critical temperature where the dislocation is perfect ($d=0$) and d_0 the low temperature stacking fault width.

The restoring force Ku is mainly due to the pinning of the dislocation loops by the remaining stacking faults. The vibrating-string model [1] leads to

$$K=\frac{12\gamma}{l^2} \tag{10}$$

γ being the line tension.

Because more and more stacking faults are eliminated when the temperature increases, the number of pinning points decreases and the mean dislocation loop length l increases. The reduction in the stacking fault area is controlled by the diffusion of W atoms which have to leave the h.c.p. structure and enter the f.c.c. solid solution. Let us assume that the dislocation loop length l increases in proportion to the diffusion coefficient of W in Co:

$$l=l_0(1+\alpha D) \tag{11}$$

α being a constant parameter and l_0 the low temperature dislocation loop length.

The internal friction Q^{-1} due to the motion of the dislocation loops in the cobalt binder phase is then given by eqn. (1) in which the relaxation strength Δ and the relaxation time τ are given by

$$\Delta=\frac{Al_0^2}{6}(1+\alpha D)^2 \tag{12}$$

$$\tau=\frac{B}{K}=\frac{c_W k d_0 l_0^2}{12\gamma}\,T\left(\frac{T_c-T}{T_c}\right)^2\frac{(1+\alpha D)^2}{D} \tag{13}$$

The function $Q^{-1}=Q^{-1}(T)$ has been drawn in Fig. 4 with the following parameters: $E=2.5$ eV, the diffusion energy of W in Co, $T_c=1073$ K, a critical temperature where the dislocation loops responsible for the peak are perfect ($d=0$), and α determined in such a way that the dislocation loop length is twice as long at 973 K. The theoretical spectrum drawn in Fig. 4 as a result of the above simple model looks like the experimental damping spectra of Fig. 1.

Because $\alpha D=1$ at 973 K, it is possible to assume that $\alpha D \ll 1$ in the peak temperature range (923 K). Consequently eqns. (12) and (13) may be simplified by

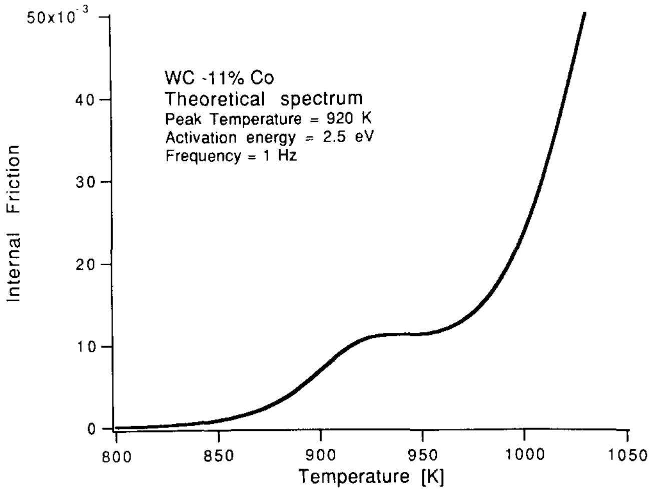

Fig. 4. Theoretical internal friction spectrum deduced from our model of dislocation damping in the cobalt binder phase of WC–Co.

setting $1+\alpha D\approx 1$ in order to determine more easily the peak temperature T_P, which is then given by $\omega\tau=1$, that is

$$\omega \frac{c_W}{12\gamma} l_0^2 d_0 \left(\frac{T_c-T_P}{T_c}\right)^2 \frac{kT_P}{D_0} \exp\left(\frac{E}{kT_P}\right)=1 \tag{14}$$

and the apparent activation energy would be given by

$$E_{\mathrm{app}}=-k\frac{\mathrm{d}(\ln\omega)}{\mathrm{d}(1/T)}=E+k\frac{3T-T_c}{T_c/T-1} \tag{15}$$

This expression of E_{app} has been reported in Fig. 2 as the theoretical curve. This curve fits rather well with the experimental data of the activation energy. This means that the real activation energy would be the diffusion energy of W in Co and that the apparent energy, which was determined from the temperature shift of the peak, increases with the temperature because the viscous force, which acts on the dislocations in the Co binder phase, decreases with the temperature. The more reliable experimental value in Fig. 2 is the point observed at low temperature by means of a forced pendulum working under isothermal conditions.

4. Discussion and conclusions

Anelastic relaxation is due to the movements of structural defects around their equilibrium position. The microstructural environment of these defects determines the relaxation strength and relaxation time. Consequently any change in the microstructure during the measurement can deeply affect these parameters and therefore the mechanical loss peak associated with the anelastic relaxation of the structural defect involved. In Fig. 5, four plots have been drawn where the internal friction is plotted as a function of the circular frequency ω and the inverse $1/T$ of the temperature. The functions $\Delta=\Delta(T)$, $E=E(T)$ and $\tau_0=\tau_0(T)$ have been chosen arbitrarily [5]. One observes in Fig. 5 that, contrary to the cases a and b where the projection of the peak summit on the $\omega-1/T$ plane is a straight line, in cases c and d the Arrhenius plot is not a straight line. Determination of the activation energy from the local slope of the Arrhenius plot (eqn. (6)) in cases c and d will give energy values which increase with temperature as was observed in WC–Co.

In conclusion, the theoretical curves of Fig. 5 as well as the experimental results obtained for WC–Co hardmetal show that the study of a high temperature relaxation peak requires a large number of measurements, if possible under isothermal conditions and as a function of frequency. A three-dimensional plot of all the results in the way depicted in Fig. 5 can provide valuable information concerning the dependence on temperature of the relaxation parameters (functions $\Delta=\Delta(T)$, $E=E(T)$ and $\tau_0=\tau_0(T)$). This information can also be very helpful for developing a microscopical model which accounts for the observed mechanical loss peak. Let us remark also that, in most of the high temperature anelastic phenomena, peak and exponential background are due to the same structural defect and therefore are not independent of each other (see Fig. 4). Consequently, it is not possible to separate the peak from the background by a simple subtraction. One needs a relaxation model.

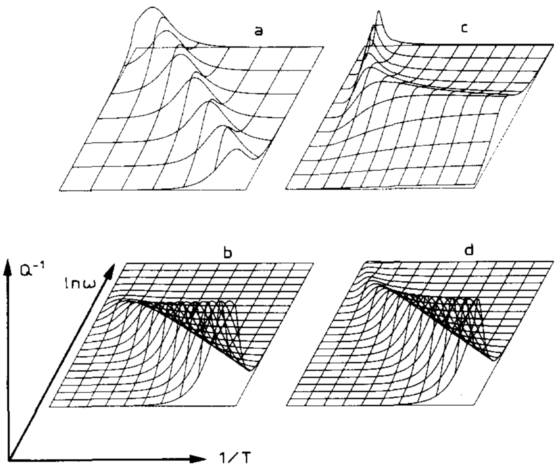

Fig. 5. Three-dimensional plot of the function $Q^{-1}=Q^{-1}(\ln\omega, 1/T)$: case a, classical mechanism (Δ, E and τ_0 are constant); case b, as for case a, but with

$$\Delta(T)=\Delta_0\frac{1}{1/T-1/T_c}$$

case c, as for case a but with

$$E=E(T)=E_0\frac{1/T_c}{1/T-1/T_c}$$

case d, as for case a but with

$$\tau_0=\tau_0(T)=\tau_0\left(\frac{1}{T}-\frac{1}{T_c}\right)$$

Acknowledgments

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References

1 A.S. Nowick and B.S. Berry, *Anelastic Relaxation in Crystalline Solids*, Academic Press, New York, 1972.

2 R. Schaller, J.J. Ammann, D. Mari and M. Maamouri, in V.K. Kinra and A. Wolfenden (eds.), *M^3D: Mechanics and Mechanisms of Material Damping, ASTM Spec. Tech. Publ. 1169,* 1992, p. 510 (ASTM, Philadelphia, PA).

3 A. Lakki and R. Schaller, *Mater. Sci. Forum, 126–128* (1993) 479.

4 R. Schaller, D. Mari, M. Maamouri and J.J. Ammann, *J. Hard Mater., 3* (1992) 351.

5 J.J. Ammann, *Thesis,* EPF, Lausanne, No. 861, 1990.

6 J.S. Zhu, R. Schaller and W. Benoit, *Phys. Status Solidi A, 108* (1988) 613.