

# Elastic After-effect in WC/Co Cemented Carbide

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## Abstract

*Free-decay internal friction measurements as a function of temperature and frequency have been used to study the inherent viscous behavior of the Co binder present at grain boundaries of a WC/Co cemented carbide material. The presence of a relaxation peak was related to the micromechanism of anelastic grain-boundary sliding and a peak-shift analysis was presented as a function of frequency. Using the mechanics of the elastic after-effect, both the viscosity and the activation energy of the intergranular Co binder could be determined. A comparison of the intergranular viscosity data was carried out with data obtained on bulk Co metal both in the high-purity state or in solid solution with a small volume fraction of WC. The viscosity of the Co binder, as determined by internal friction, showed good agreement with the bulk Co/WC solid solution, whose chemical composition was presumably the closest to the intergranular binder in the cermet material. Based on the agreement between intergranular and bulk viscosities as well as activation energy values, it is considered that the present method can be more generally used in ceramic/metal materials. © 1999 Elsevier Science Limited. All rights reserved*

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## 1 Introduction

Zener<sup>1</sup> has predicted the possible anelastic deformation of a polycrystal with assuming that the shear resistance of internal grain boundaries obeys the viscosity law commonly associated with amor-

phous materials. Kê<sup>2</sup> found experimentally that this anelastic effect actually occurs in polycrystalline metals and proved that it is due to microscopic and reversible slip of their grain boundaries. The microscopic mechanism responsible for anelasticity of polycrystalline solids has been denominated *elastic after-effect*. Upon increasing the temperature, the grain boundaries may cease to be tightly bonded and behave in viscous fashion. In this case, two main consequences are recognized: (i) microscopic shear stresses cannot be transmitted across grain boundaries, thus the elastic deformation of crystalline grains (in response to an external stress) will produce local grain-boundary sliding; and (ii) a finite time has to be elapsed for such a microscopic shear deformation of grain boundaries to occur or to be recovered, due to the finite viscosity of grain boundaries. After releasing the external stress, a recover effect may occur which is due to the microscopic (elastic) back-stress exerted by the crystalline grains. Viscous sliding is thermally activated according to the change in grain-boundary viscosity upon temperature.

Clear evidences supporting the Zener's theory of anelasticity and the elastic after-effect can be provided by testing the temperature dependence of low-frequency internal friction in ceramic polycrystals.<sup>3–8</sup> The anelastic grain-boundary sliding effect is revealed by the presence of a relaxation peak (referred to as grain-boundary peak henceforth) whose top temperature shifts towards higher temperatures with increasing the frequency of the internal friction measurement. Common to many ceramics is the presence of a low-melting glass phase, usually segregated at triple-grain pockets and/or along thin intergranular films.<sup>9</sup> It has been shown<sup>3–8</sup> that the viscosity of the intergranular film can be quantitatively related to the top-temperature of the grain-boundary peak of internal friction. The outcome of this analysis enables one to

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determine both the magnitude of the intergranular glass viscosity and its activation energy. The physical circumstance according to which the *elastic after-effect* (i.e. the internal friction peak) can manifest in polycrystalline ceramics resides in the marked difference of melting point between the intergranular glass and the crystal grains. In other words, the viscous softening of the glass at grain boundaries can occur in a temperature range in which the bulk ceramic grains still behave elastically and, thus, can provide the back-stress which will recover local grain-boundary sliding upon releasing the external stress.

Purpose of this paper is to characterize the elastic after-effect in a different class of polycrystalline ceramics: those bonded by a metallic phase (simply referred to as cemented carbides henceforth). The anelastic grain-boundary sliding effect and, thus, the presence of a relaxation peak of internal friction can still be expected in these materials because of the marked difference of melting point between the metal phase at grain boundaries and the bulk ceramic grains. Thus, as in the case of glassy bonded ceramics, it should in principle be possible to determine the viscosity of the intergranular (metal) phase using the elastic after-effect. A crystalline metal phase is expected to possess a sharp viscosity drop down near the melting point. Nevertheless, with increasing temperature below the melting point, a continuous reduction of viscosity should occur, as in the case of an amorphous intergranular film. We expect that this latter viscosity characteristic can be revealed by a peak-shift analysis performed as a function of frequency in the internal friction measurement.

## 2 Experimental Procedure

The cermet material used in the present internal friction study was a WC/Co material which was provided by Pozzo Co., International Saws (Udine, Italy). It contained a volume fraction of Co metal binder  $\approx 6$  wt% (i.e.  $\approx 11$  vol%). A major impurity of free carbon was present for  $\approx 0.2$  wt%. Micrographs showing the microstructure of the present WC/Co material have been given in a previous report.<sup>10</sup> The average size of the WC matrix grains was  $1.5 \mu\text{m}$ . The average thickness of the metal Co binder was determined from analysing a series of SEM pictures and found to be  $\delta = 0.3 \mu\text{m}$ . The WC/Co material was thought to be suitable for the present internal friction investigation since the melting point of Co metal (i.e.  $T_m = 1766 \text{ K}$ <sup>11</sup> and  $1548 \text{ K}$  in the presence of free C) is rather low as compared to the highly refractory WC phase. In addition, the Co phase in this cemented carbide continuously wets the

WC grains, thus providing a model microstructure suitable for basic studies. This point will be better explained in the theoretical assessment of the elastic after-effect given in the next section.

The apparatus utilized for measuring concurrently internal friction,  $Q^{-1}$ , and shear modulus,  $G$ , was a torsional pendulum enclosed in a vacuum-tight system in which a controlled Ar atmosphere was maintained throughout the experiments. A complete draft of this torsional pendulum has been shown in a previous paper.<sup>12</sup> Internal friction was measured as a function of both temperature and frequency.  $Q^{-1}$  data were automatically collected at intervals of 5 K according to the free-decay method. Experiments were conducted in the frequency range of 1–27 Hz on rectangular specimens of  $2 \times 3 \times 50 \text{ mm}$  in dimensions. High temperature was reached during torsional vibration by circumventing the specimen with a carbon heater, while a thermocouple and an infrared thermo-analyzer was used for detecting temperature. Preliminary calibrations performed with blank tests on the torsional pendulum apparatus dictated a minimum length of the specimen  $> 45 \text{ mm}$ . The shear modulus of the materials,  $G$ , was measured simultaneously to internal friction, according to the resonance vibration method.

## 3 Theoretical Assessment

### 3.1 Elastic after-effect in WC/Co cemented carbide

Intergranular phases in polycrystalline ceramics are source of internal friction arising from the viscous slip which takes place across grain boundaries at elevated temperatures. The mechanism of microscopic sliding accompanied by internal stress relaxation at grain boundaries is schematically shown in Fig. 1. It is expected that while, with increasing temperature, the metal phase softens and becomes viscous, the highly refractory WC ceramic grains behave in an elastic fashion. These physical circumstances are represented by the dashpot at the interface and by the elastic springs within the ceramic grains, respectively, as depicted in Fig. 1. Since the viscous grain boundaries cannot sustain the externally applied shear stress, local slip will occur until the local grain-boundary stress has been released. Provided that no local damage has occurred at grain boundaries, the elastic grains will push back the grain boundaries to their original position when the external stress is released, with the result that the polycrystalline structure will be restored to its original undeformed state. Such an elastic back-stress arises from constrained grain-boundary slip and produces anelasticity (i.e. the so called elastic after-effect). Due to the viscosity of

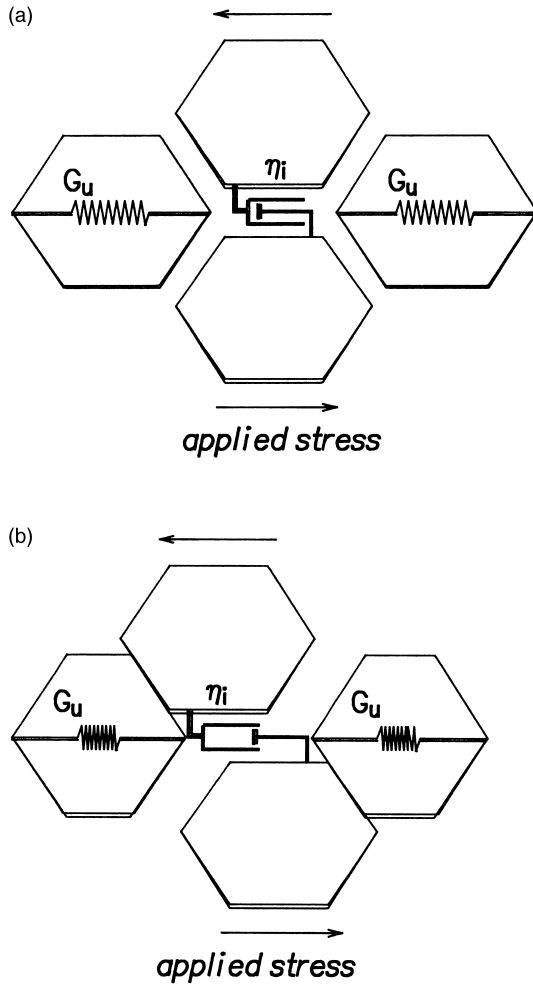


Fig. 1. Schematic of the elastic after-effect.

the metal phase at grain boundaries, a finite time will be needed to recover internal grain-boundary slip. The anelastic effect of grain-boundary sliding gives rise to a peak in the internal friction versus temperature curve. Hereafter, the case of a macroscopic shear stress applied as a sinusoidal pulse wave (maximum stress,  $\tau$ ) is considered.

The pulse stress activates the microscopic (elastic) displacement of the ceramic grains, namely of the elastic springs in Fig. 1, the polycrystal starting to oscillate at a given torsional frequency,  $f_0$ . In absence of external frictions, viscous grain boundary sliding will produce internal energy dissipation in the specimen. Accordingly, the amplitude of the free torsional oscillation will reduce due to such an internal viscous slip. The internal friction,  $Q^{-1}$ , is a dimensionless parameter which measures the rate of internal energy dissipation. It is defined as the logarithmic decrement of the free oscillation of the polycrystal taking place subsequently to the initial pulse stress:<sup>13</sup>

$$Q^{-1} = (1/\pi) \ln(A_n/A_{n+1}) \quad (1)$$

where the argument of the natural logarithm represents the ratio of amplitude ( $A$ ) in two successive

free oscillations ( $n$  and  $n + 1$ ), the higher the ratio the higher the internal energy dissipation.

Two parameters can enhance the rate of internal energy dissipation,  $Q^{-1}$ . They are: (i) the length over which the reciprocal sliding between grains occurs,  $\Delta u$ , and, (ii) the intrinsic viscosity,  $\eta_i$ , of the glassy grain-boundary film. An increase of  $\Delta u$  will produce a higher rate of energy dissipation as well as a decrease of  $\eta_i$  will lead to a decrease of such a rate. It is now important to consider the variation of  $\Delta u$  and  $\eta_i$  with increasing temperature. At low temperatures (e.g. at ambient temperature) the intergranular phase behaves as a solid and can transmit the applied shear stress across adjacent grains. Thus no viscous sliding and no internal energy dissipation can occur. In this case, the  $Q^{-1}$  value is minimum. When temperature increases, the viscosity of the grain-boundary phase,  $\eta_i$ , starts decreasing and slip occurs. However, the reciprocal slip of the grains will require a certain finite time to take place and, if the frequency/amplitude of the pulse is fixed, the boundary may have virtually no time to slide at intermediate temperatures. In other words, if the viscosity of the grain-boundary film is still sufficiently high, the actual displacement  $\Delta u$  may be very limited and the energy dissipation in the polycrystal be low. Obviously, the magnitude of  $\Delta u$  will gradually increase with decreasing  $\eta_i$  (i.e. with increasing temperature). Consequently, also the  $Q^{-1}$  value will increase until the maximum  $\Delta u$  value allowed by the elastic displacement of neighboring grains will be reached. This will occur at a certain characteristic temperature,  $T_p$ , for which viscous sliding will experience the maximum intergranular displacement,  $\Delta u_{\max}$ , exactly within the characteristic time  $t^* = 1/2\pi f_0$ . With a further increase of temperature (i.e. for each  $T > T_p$ ), the maximum displacement  $\Delta u_{\max}$  will be systematically exploited but, since the intergranular phase viscosity will decrease, the energy dissipation rate will experience a monotonic decrease. This mechanism can explain the presence of a peak of internal friction centered at a temperature  $T_p$ . The maximum (elastic) displacement allowed by the neighboring grains is proportional to the average grain size,  $d$ , and to the elastic shear strain,  $\gamma = \tau(1 - \nu)/G$ , where  $\nu$  and  $G$  are the Poisson's ratio and the shear modulus of the bulk ceramic crystallites, respectively. Thus, if we assume that  $G = G_u$ , namely the unrelaxed (or the room-temperature) modulus of the polycrystal,  $\Delta u_{\max}$  can be written as:<sup>14</sup>

$$\Delta u_{\max} = \alpha d \tau (1 - \nu) / G_u \quad (2)$$

where  $\alpha$  is a proportionality constant related to the morphology of the ceramic grains and the grain boundaries.<sup>14</sup> Under the hypothesis that the

grain-boundary film is continuously wetting the grains, a basic equation of viscosity in lubricated channels may apply to give, through the use of eqn (2), a viable equation for calculating the grain-boundary viscosity,  $\eta_i$ , at the peak-top temperature,  $T_p$ .<sup>15</sup>

$$\eta_i = \tau \delta (t^*/\Delta u_{\max}) = G_u \delta / 2\pi f_0 \alpha (1 - \nu) d \quad (3)$$

where  $\delta$  is the grain-boundary thickness and  $t^* = 1/2\pi f_0$  is the characteristic time for sliding to occur over the maximum excursion allowed by the neighboring grains. Equation (3) in principle enables one to evaluate the inherent grain-boundary viscosity in a ceramic polycrystal, provided that two parameters related to the microstructural characteristics of the material are evaluated: (i) the grain-boundary film thickness,  $\delta$ ; and, (ii) the morphology factor,  $\alpha$ , *a priori* unknown. The grain-boundary thickness is usually estimated from quantitative electron microscopy,<sup>9</sup> while the morphology parameter,  $\alpha$ , can be expressed in terms of experimentally accessible parameters, according to the following considerations. The total macroscopic shear strain,  $\gamma$ , of a polycrystal loaded at the peak-top temperature by an externally applied shear stress,  $\tau$ , is given by the sum of an elastic component and an anelastic component according to the relation:

$$\gamma = (\tau/G_u) + (\Delta u_{\max}/d) = \tau/G_R \quad (4)$$

where  $G_u$  is the unrelaxed shear modulus of the ceramic polycrystal which is again assumed to equal the modulus of the bulk grains,  $G$ , because, at room temperature, the intergranular phase fully transmits shear stress across adjacent grains. This assertion is however valid only when the overall volume fraction of grain-boundary phase in the polycrystal is small.  $G_R$  is the macroscopic shear modulus of the 'relaxed' polycrystal at the peak-top temperature. The relaxation is thought to entirely arise from a viscous grain-boundary slip process. Substituting and rearranging from eqns (2) and (4), the morphology factor  $\alpha$  can be expressed as:

$$\alpha = [(G_u/G_R) - 1]/(1 - \nu) \quad (5)$$

where the relaxation modulus ratio,  $G_u/G_R$ , at the peak-top temperature is now an experimentally accessible parameter. Eliminating  $\alpha$  between eqns (4) and (5), one obtains:

$$\eta_i = (1/2\pi f_0)(\delta/d)\{G_u/[(G_u/G_R) - 1]\} \quad (6)$$

Equation (6), valid only at the temperature  $T = T_p$ , represents the basic relation which links the measured internal friction characteristics to the intrinsic grain-boundary viscosity. This equation

will be used in the results and discussion section for calculating the grain-boundary viscosity from internal friction measurements.

### 3.2 Internal friction of the bulk Co metal

High-temperature internal friction and elastic modulus changes of cobalt were measured by Kamel and Botros<sup>16</sup> at a frequency  $\approx 10$  Hz. Amman *et al.*<sup>17</sup> also reported about the internal friction of a solid solution of 11 wt% WC in Co. Literature data for both pure Co and Co/11 wt% WC solid-solution are plotted in Fig. 2. As seen, the internal friction of high-purity polycrystalline Co in well-annealed state is simply represented by an exponential-like background. In pure Co, no anelastic peak is found due to grain-boundary sliding as reported in other polycrystalline metals (for example, Al<sup>18</sup>). An internal friction peak in Co is detected at a relatively low temperature (i.e.  $\approx 410$  K at 11.7 Hz) in quenched samples due to point-defects relaxation.<sup>16</sup> This peak is not considered in the present high-temperature investigation. In addition, a further internal friction peak, found in pure Co at  $\approx 700$  K, has been related to the martensitic phase transition from hexagonal crystal structure to cubic face-centered structure (hcp $\leftrightarrow$ fcc).<sup>19</sup> However, martensitic transformations only occur during fast cooling where a normal diffusion transformation cannot take place. Amman *et al.*<sup>17</sup> have investigated the structure of the Co phase present in WC/Co cemented carbides and found that the structure of the binder Co phase remains fcc up to temperature above 1300 K. For this reason, the effect of phase transformation on the internal friction behavior of WC/Co cemented carbide will be neglected in the present investigation.

A simple background trend is also found for the internal friction curve of a solid-solution Co/WC.

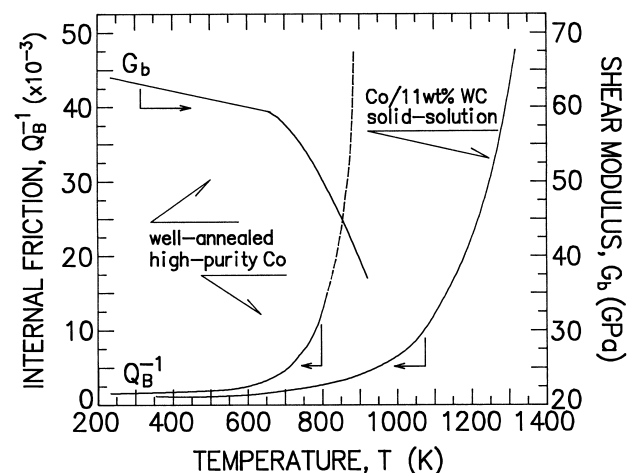


Fig. 2. Dependence on temperature of internal friction and shear modulus of high-purity Co<sup>16</sup> and Co/11 wt% WC solid-solution,<sup>17</sup> measured at around 10 Hz.

The absence of the phase transition peak in Co/WC solid solution confirms that W and C impurities inhibit the Co-phase transformation. However, the background curve (recorded at a comparable frequency) is markedly shifted toward higher temperatures, as compared to pure Co. Assuming that the Co/WC solid solution have a chemical composition similar to that of the binder phase of WC/Co cermet, the background curve of the Co/WC alloy is considered to be representative of the bulk internal friction behavior of the Co phase present at the grain boundaries of the WC/Co material.

In polycrystalline metals and metallic alloys,<sup>20,21</sup> the viscoelastic background of internal friction may arise both from the intrinsic plastic deformation of individual grains and from the build up of stress at the grain edges enhancing local grain-boundary diffusion. These mechanisms are also considered to cause irrecoverable (plastic) creep of a linear and thermally activated type. It is beyond the scope of this paper to discuss the origin of the viscoelastic background component of internal friction in Co and related alloys. We shall limit our treatment to a rheological view which relates the (background) internal-friction curve to the macroscopic viscosity of the bulk metals,  $\eta_b$ . Such a bulk viscosity constitutes an important parameter to be compared to the intergranular viscosity,  $\eta_i$ , of the WC/Co polycrystal.

In absence of anelastic peaks, the Co (or Co/WC solid-solution) polycrystal can be considered to be a Maxwell-like solid, whose macroscopic viscosity,  $\eta_b$ , is related to the internal friction background component,  $Q_B^{-1}$ , as:<sup>13</sup>

$$Q_B^{-1} = (G_b/2\pi f_0)(1/\eta_b) \exp(-E_b/kT) \quad (7)$$

where  $G_b$  and  $T$  are the shear modulus of bulk Co and the measurement temperature, respectively;  $E_b$  is an activation energy associated to the elementary phenomenon which originates the internal friction background of Co.

#### 4 Results and Discussion

Figure 3 shows the internal friction curve of the WC/Co cemented carbide recorded as a function of temperature at the frequency of 16 Hz. The curve is represented by the superposition of an anelastic peak component, centred at about 940 K, and an exponential-like background of viscoelastic origin. These two components are also shown in Fig. 3, after deconvolution of the experimental curve. The trend of the internal friction curve is similar to that usually found in polycrystalline ceramics with a

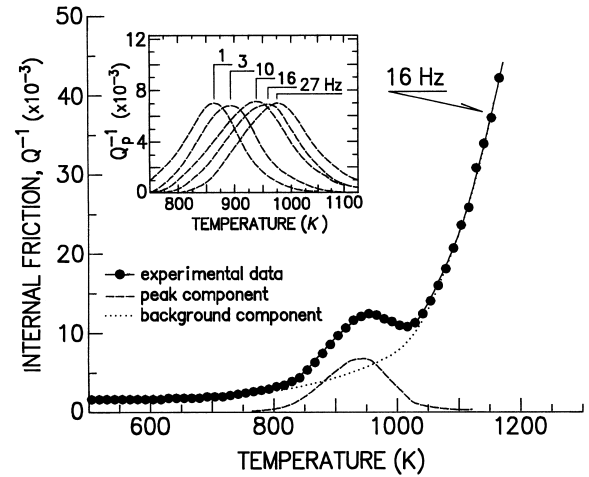


Fig. 3. Internal friction (measured at 16 Hz) of WC/Co cemented carbide as a function of temperature. The experimental curve is deconvoluted in an anelastic peak and a viscoelastic background component. In the inset is shown the shift of the peak component as a function of the applied frequency, as measured in the range 1–27 Hz.

glass-phase film wetting the grain boundaries.<sup>3–8</sup> Thus, similar to glass-phase-bonded ceramics, it can be thought that the peak component of the present cemented carbide is related to anelastic grain-boundary sliding through the elastic after-effect mechanism. To prove this assertion, internal friction experiments were repeated at different oscillation frequencies. The internal friction peak component,  $Q_p^{-1}$ , obtained by successive experimental runs was found to consistently shift with frequency, the higher the frequency the higher the temperature of the anelastic peak. As explained in Section 3.1, at the temperatures of the peak maxima, the characteristic time, within which anelastic grain-boundary sliding occurs, should exactly equal the unitary time,  $t^* = 1/2\pi f_0$ , dictated by the measurement frequency. Thus, the intrinsic viscosity of the intergranular binder Co can be calculated according to eqn (6), provided that the modulus relaxation ratio,  $G_R/G_u$ , (namely the grain-boundary morphology factor,  $\alpha$ ) is measured. Figure 4 shows the variation of the modulus relaxation ratio,  $G_R/G_u$ , as a function of temperature in correspondence of the temperature interval of the peak of internal friction. A value  $G_R/G_u \approx 0.95$ , corresponding to  $\alpha \approx 0.06$ , can be estimated from the experimental curve. Using this value and the intergranular binder thickness,  $\delta \approx 0.3 \mu\text{m}$ , the intrinsic viscosity,  $\eta_i$ , of the intergranular Co binder can be calculated according to eqn (6). The results of this calculation are shown in the Arrhenius plot of Fig. 5, from which an apparent activation energy of  $\approx 70 \text{ kJ mol}^{-1}$  is found. In this context, it can be interesting to compare the intrinsic viscosity of the intergranular Co binder with the bulk viscosity,  $\eta_b$ , of both the high-purity Co metal and the Co/WC solid solution. Using eqn

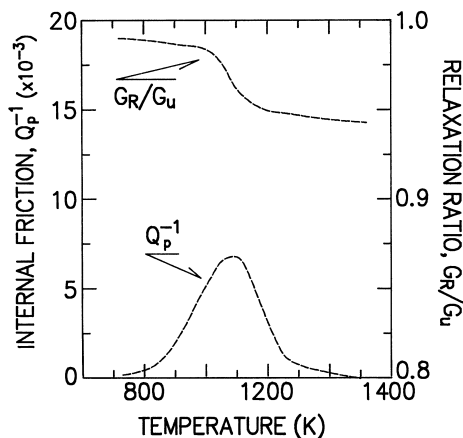


Fig. 4. Relaxation modulus ratio,  $G_R/G_u$ , as a function of temperature in the interval of temperature at which the internal friction peak appears at 16 Hz.

(7) and the  $Q_B^{-1}$  and  $G_b$  data in Fig. 2, the bulk viscosities below the melting point of both high-purity Co and Co/WC solid-solution can be calculated from internal friction data. The results of this calculation are also shown in Fig. 5. The intrinsic viscosity of the intergranular Co is closer to that of the Co/WC solid-solution than to pure Co metal. This is due to the presence of free-carbon in the binder and, thus, the similar chemical composition of the Co binder to the bulk Co/WC alloy. Good agreement is also found in comparing the activation energy of viscosity change between the intergranular and the bulk metal phases (cf. Figure 5).

Although the internal friction behavior of the WC/Co cemented carbides has been previously reported by other investigators<sup>17</sup> and a peak component detected with characteristics similar to those found in the present investigation, a discussion in terms of anelastic grain-boundary sliding has not been yet given. In this paper, we have

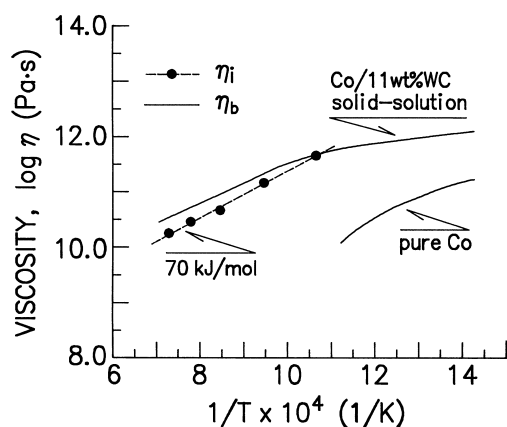


Fig. 5. The intrinsic viscosity,  $\eta_i$ , of the intergranular Co binder in the WC/Co cemented carbide material is calculated from the internal friction data in Fig. 3 [i.e. according to eqn (6)] and compared to the macroscopic viscosity,  $\eta_b$ , of bulk high-purity Co and Co/11 wt% WC solid-solution. Bulk viscosity data for the two metals were obtained from the internal friction in Fig. 2, according to eqn (7).

provided evidence that the anelastic peak component is related to the reciprocal slip of adjacent grains through the mechanism of elastic aftereffect, as predicted by Zener.<sup>1</sup> This microscopic mechanism can be used to measure the intrinsic viscosity of the metallic binder, as proved by the good agreement between  $\eta_i$  and  $\eta_b$ , shown in Fig. 5. The quantitative determination of intrinsic viscosity of the metal grain-boundary phase in cemented carbide materials through internal friction characterization is conceptually similar to that of the viscosity of the intergranular glass phase in ceramics.<sup>4</sup> The measurement of a microscopic structural parameter, like as the intrinsic binder viscosity,  $\eta_i$ , may allow to better understand the high-temperature deformation behavior of ceramic/metal composites. In fact, the knowledge of the  $\eta_i$  parameter enables to construct and to quantitatively use a mechanical analogue which can predict with some accuracy the primary creep and the steady-state deformation of polycrystalline ceramics.<sup>22</sup>

## 5 Conclusion

The viscosity of the intergranular Co binder has been quantitatively evaluated in a WC/Co cemented carbide using internal friction measurements as a function of both temperature and frequency. Similar to glass-bonded ceramics, the cemented carbide material showed an internal friction peak, whose temperature shift as a function of frequency could be related to the viscosity change of the intergranular metal phase. Using the equations governing the mechanics of elastic aftereffect, the intrinsic viscosity of the Co binder has been determined as a function of temperature and compared with that of bulk pure Co metal and Co/WC solid-solution. Both the viscosity value and the activation energy for the viscosity change of the Co binder were very close to that of the bulk Co/WC solid solution, showing that the assessment by internal friction of the intergranular metal viscosity in the ceramic/metal composites leads to physically sound results. It is thus suggested that the present internal friction method, capable of quantitatively determining the intergranular viscosity of polycrystalline ceramics, can be more generally applied to other ceramic/metal composites and used for the rheological modelling of their deformation behavior.

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