

Penetration kinetics of liquid sulphides in nickel and cobalt

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Abstract

The penetration of liquid sulphides into polycrystalline nickel and cobalt was studied as a function of temperature (between 750 and 1100°C) and time.

It was found that the penetration is faster for nickel than for cobalt, that the process is governed by volume diffusion with an activation energy of about 75 kJ/mol.

A relationship exists between the dihedral angle formed by the liquid along the grain boundaries and the penetration rate.

Riassunto

Cinetica della penetrazione di solfuri liquidi in nichel e in cobalto

Viene presentato uno studio sulla penetrazione, in funzione del tempo, di solfuri liquidi ai giunti di grano di nichel e cobalto policristallini, in un campo di temperatura tra i 750 e i 1100°C.

Si è trovato che la penetrazione è più rapida nel caso del nichel che per il cobalto, che il processo è governato dalla diffusione in volume e la sua energia di attivazione è di circa 75 KJ/mol.

Si dimostra infine che esiste una relazione tra l'angolo diedro, formato dal liquido ai giunti di grano, e la velocità di penetrazione.

Introduction

Aggressive environments, which ordinarily contain sulphur, form, on structural steels and superalloys, corrosion products whose composition and growth mechanism are, today, extensively studied and fairly well known (1-3).

It happens, sometimes, that these compounds are in the liquid state, depending on the temperature and on the composition of the gaseous atmosphere. This means that the attack of the solid alloy follows specific laws and is particularly severe along grain boundaries. When a polycrystalline alloy is held in equilibrium with a saturated liquid phase, grooves will develop at the intersection of the solid/liquid interface and the grain boundaries, as sketched in Fig. 1. The equilibrium root angle 2ϕ (dihedral angle) is linked to the solid/liquid interfacial tension σ_{sl} and to the grain boundary tension σ_{gb} by the Smith's relationship (4)

$$\sigma_{gb} = 2 \sigma_{sl} \cos 2\phi \quad (1)$$

Moreover the grooves deepen and widen with time, due to the mass transport originated by the difference in chemical potential between the flat interface (μ_{∞}) and the points of the curved interface of the groove (μ). This difference is expressed by the Gibbs-Thompson equation

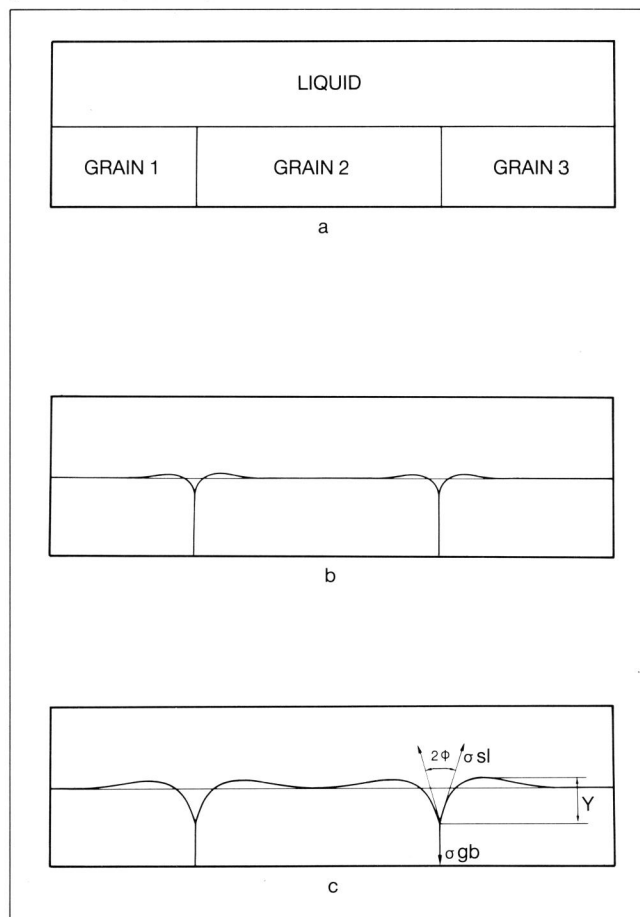
$$\mu = \mu_{\infty} + K \sigma_{sl} V \quad (2)$$

where K is the curvature at the point considered and V the molar volume of the solid.

The concentration gradient along the interface leads to a transfer of atoms of the solid phase from the groove root to the flat interface. In this way the groove grows maintaining its shape, according to kinetic laws firstly

established by Mullins (5,6).

Fig. 1 - Grooving of a polycrystalline metal as a function of time: a) $t = 0$; b) grooves develop; c) steady state.



These laws offer the possibility of establishing the type of diffusion process and, in principle, of measuring either the diffusion coefficient or the interfacial tension value.

In the present paper an analysis of the penetration kinetics of the liquid sulphides in polycrystalline nickel and cobalt is presented, in a temperature range between 750 and 1100 °C. The kinetic data are then related to the equilibrium groove angle and to the values of solid/liquid and grain boundary tension. A calculation of the activation energies for the penetration of the liquid sulphides into the solid metals will also be presented together with an evaluation of the kind of diffusion process taking place at the solid/liquid interface.

Experimental

Rectangular Ni and Co specimens, 10 × 15 × 2 mm, (99.999% nominal purity) were ground on both faces and then annealed under vacuum at 900°C for 3 h (nickel) and at 600°C for 4 h (cobalt) in order to eliminate texture effects due to rolling.

After this treatment the specimens were given a final polishing in order to obtain planar surfaces.

Similar specimens, previously treated in a pure sulphur atmosphere, and thus covered by a thin sulphide layer, were lightly ground and then placed in contact with the two sides of the testpiece. In this way a sandwich structure was obtained, where the metal was in contact, at the test temperature, with its saturated liquid sulphide.

All the runs were made in a pre-evacuated silica reaction chamber. After each run, the specimens were quenched by withdrawing the test tube from the furnace and then prepared, by standard techniques, for optical microscopy.

The depth of each groove was measured using the rotating stage of the microscope, at a magnification of about X 1000. Particular care was taken to identify the position of the plane, undisturbed interface and to measure symmetrical grooves, perpendicular to the interface.

Theoretical background

Grain boundary grooving may occur, under isothermal conditions and with bulk phases in equilibrium, by three different processes: evaporation-condensation, surface diffusion or volume diffusion. The theoretical analysis of the grooving process (5,6) rests on the following fundamental hypothesis:

- the interfacial tension is independent of crystallographic orientation;
- the diffusion processes are in a quasi-steady state;

the time necessary for the diffusion is short as compared with the time necessary for a change in the interfacial shape;

- the fluid solution is considered an ideal one;
- gravity-driven convection is negligible;
- the interface is initially perfectly plane: during the penetration of the liquid phase the groove root has a slight slope relative to the initial flat interface.

Under these assumptions, the following equations are found, relating the depth of the groove, Y , to the time, t .

$$Y = 1.01 m (At)^{1/3} \text{ volume diffusion} \quad (3)$$

$$Y = 0.973 m (Bt)^{1/4} \text{ surface diffusion} \quad (4)$$

$$Y = -1.13 m (Ct)^{1/2} \text{ evaporation-condensation} \quad (5)$$

where m is the slope of the groove at its root ($X = 0$) and the parameters A , B and C are related to well known physical and chemical properties by the following relationships:

$$A = (C_o \sigma_{sl} V^2 D_v) / (kT) \quad (6)$$

$$B = (\sigma_{sl} V^2 N D_s) / (kT) \quad (7)$$

$$C = (\sigma_{sv} V^2 P_o) / [(2 \pi m)^{1/2} (kT)^{3/2}] \quad (8)$$

where

C_o is the equilibrium concentration on the plane surface,

V is the atomic volume,

D_v , D_s are the volume and surface diffusion coefficients,

P_o is the equilibrium pressure on the flat surface,

N is the number of atoms per unit surface,

T is the temperature and k is the Boltzman constant.

On the basis of these results it is clear that a single plot of $\log Y$ vs. $\log t$ can give the value of the exponent of the kinetic law. On the other hand, knowledge of the factor A (or B , or C) could lead to the evaluation of the specific diffusion coefficient or, alternatively, of the interfacial tension. However, this last point is, in practice, very difficult to apply, because the usual scatter of the experimental points prevents a sufficient precision being reached in determining the A (B or C) value.

It is also worth mentioning that the mathematical analysis which leads to the relationships written above, allows the drawing of the (normalized) profile of the groove in the three cases. As shown in Fig. 2, when volume or surface diffusion occurs, humps are present above the original flat surface, being more pronounced in the case of surface diffusion. As the shape of the groove is not time dependent, it is often sufficient to examine its trace on a metallographic section of the specimen in order to find a first indication of the type of

diffusion process which has occurred at the interface.

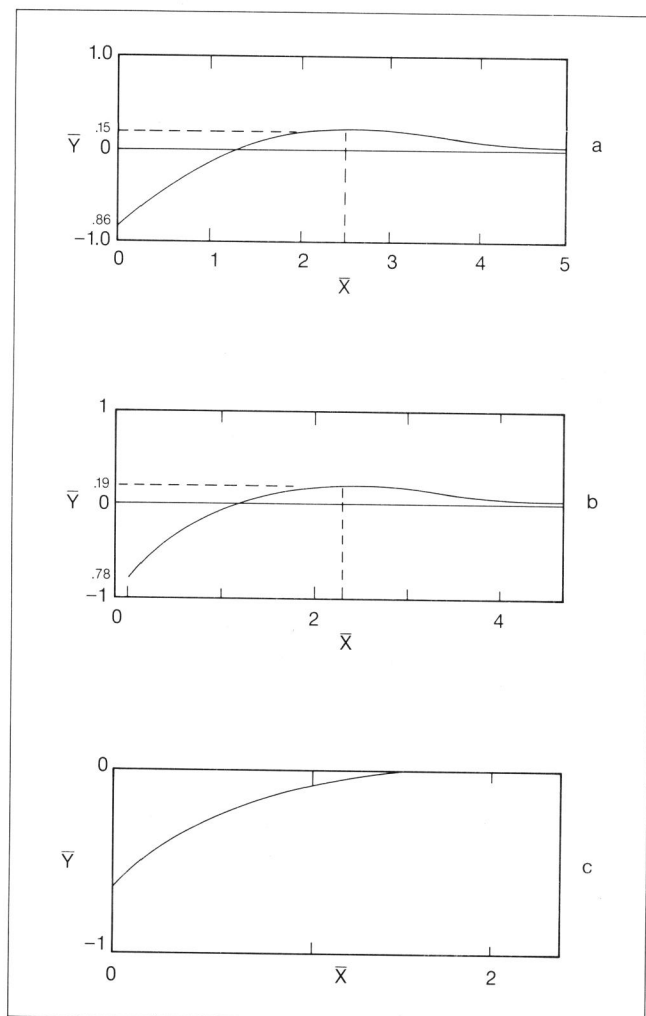


Fig. 2 - Grooves profiles, after Mullins, in the case of:
a) volume diffusion; b) surface diffusion; c) evaporation-condensation
 \bar{x} and \bar{y} are normalized coordinates.

Experimental results and analysis

In Fig. 3 the dihedral angle vs. time is reported (7) for Ni-S and Co-S systems. They were obtained under equilibrium conditions in pure sulphur and will be used as important parameters in the next discussion. The results of the penetration test, performed with holding times up to 70 h, are presented in Figs. 4 and 5. In these diagrams a rather large uncertainty is assigned to each experimental measurement. This is because the polycrystalline specimens used had grains randomly orientated and grain boundaries not always exactly perpendicular to the interface. For this reason a

Fig. 3 - Variation of the equilibrium dihedral angle with temperature (after Ref. 7)
a) Ni-S; - b) Co-S.

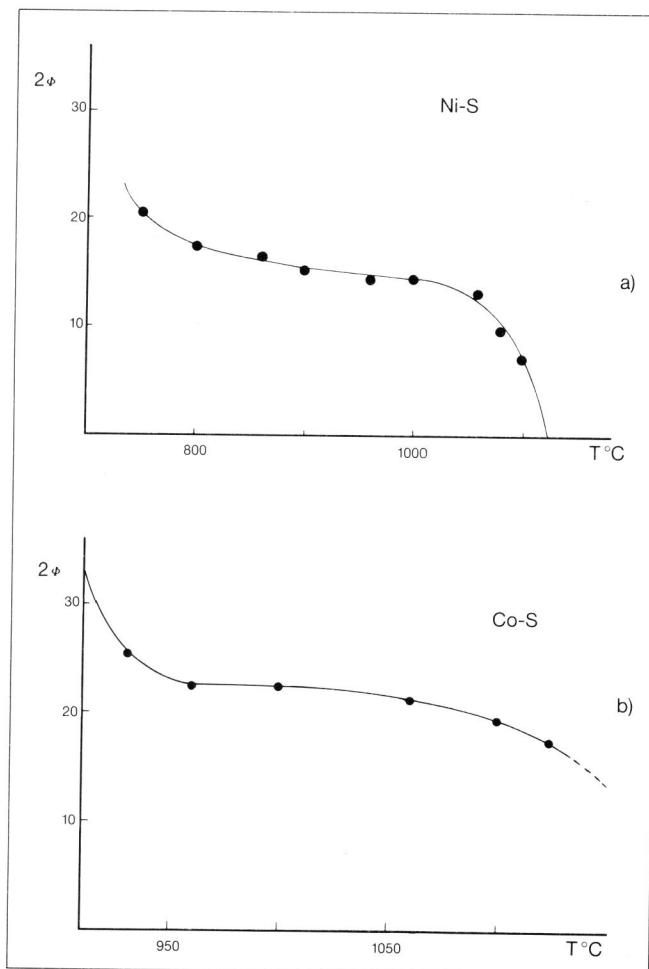
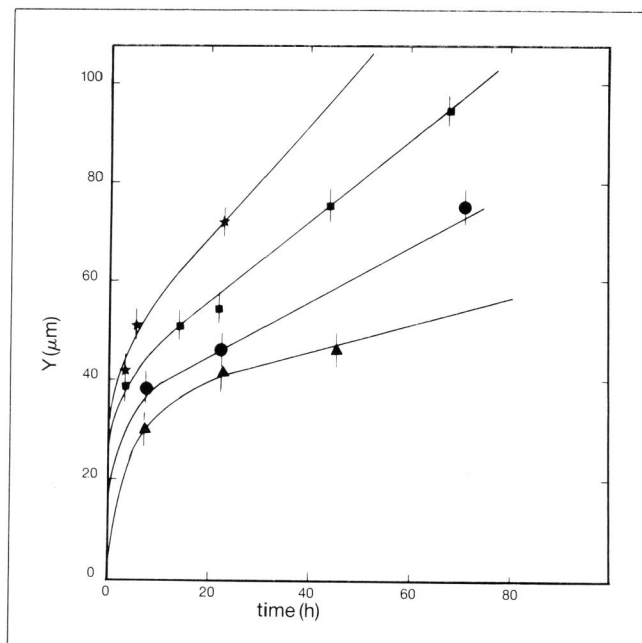


Fig. 4 - Depth of penetration as a function of time; Ni-S system
▲ = 750°C; ● = 850°C; ■ = 900°C; ★ = 1000°C.



large number of grooves were measured on each specimen (typically 100) and the mode of the statistical distribution of measured groove depth was taken as the true depth. A least square fitting was made on the set of points at each temperature and the resulting slope was calculated.

This slope, which is equal to $1/n$, the exponent in Eqs. 5-6, results, in general, near to $1/3$ except for nickel at low temperatures, where it is nearer to $1/4$.

A typical groove profile is presented in Fig. 6, where the characteristic humps are clearly visible.

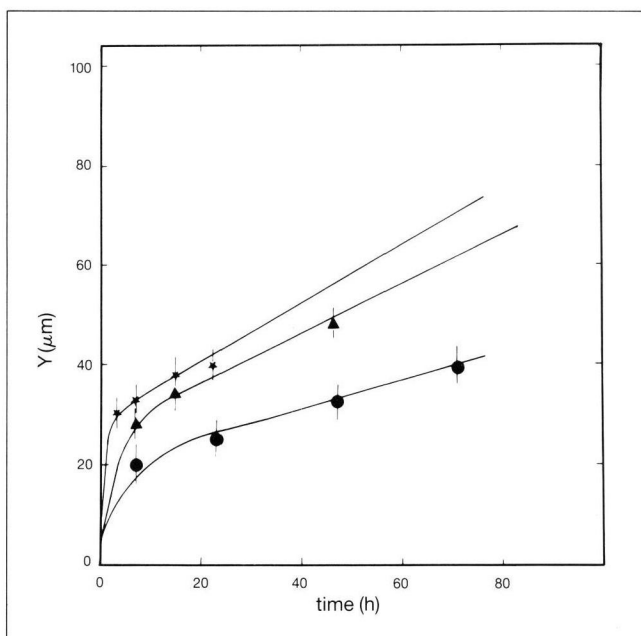
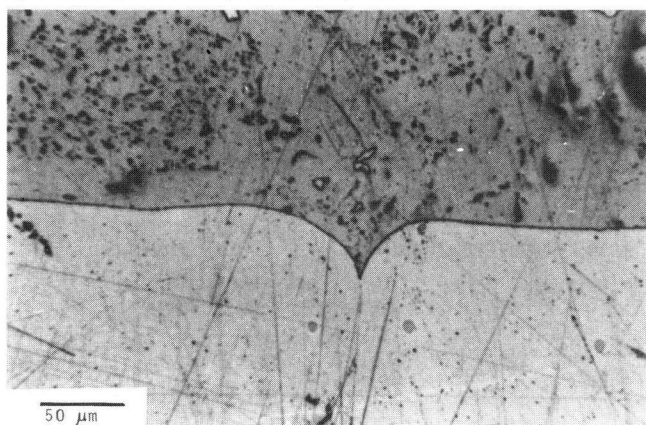


Fig. 5 - Depth of penetration as a function of time; Co-S system.
■ = 930°C; ▲ = 1000°C; ★ = 1060°C.

Fig. 6 - Groove profile. Ni-S system at 750°C., 23 h.



The rate constant of the grooving process depends on temperature, increasing with it. It is then possible to make an estimate of the activation energy of the diffusion process. In order to do this, the Arrhenius method may be used, which consists in determining the kinetic law best fitting the experimental points. The "rate constant" K of this law follows the general relationship

$$K = K_0 \exp(-E/RT) \quad (9)$$

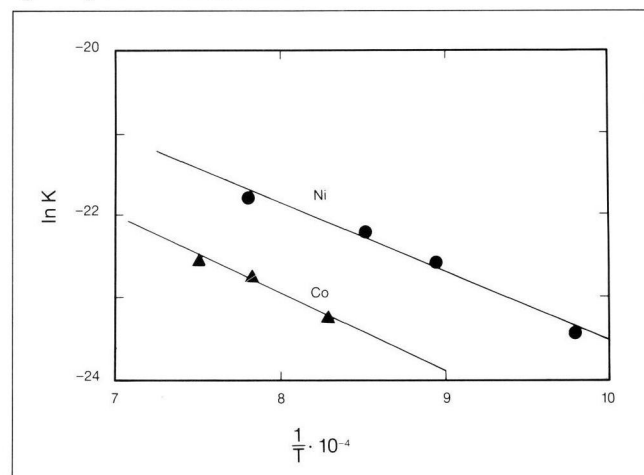
where E is called the "activation energy" of the process.

In our case, from Figs. 4 and 5 it is possible to see that a linear law is a very good approximation in the second part of the diagram, that is for times longer than 25-30 h. Based on this assumption the diagram in Fig. 7 is obtained, indicating the following values for the activation energies:

$$\begin{aligned} \text{Ni-S} \quad E &= 70 \text{ kJ/mol} \\ \text{Co-S} \quad E &= 75 \text{ kJ/mol} \end{aligned}$$

The same results would be obtained by using Mullins equations over the whole temperature range. In our case this procedure is somewhat questionable, mainly because the exponent of the kinetic law varies significantly from low to high temperatures, mainly for the nickel-sulphur system. In fact, for the Co-S system, where the ΔT is fairly limited, and $1/n$ has more constant values, a figure $E = 84 \text{ kJ/mol}$ can be computed, in agreement with the previous calculations, while, for the Ni-S system, a value $E = 10 \text{ kJ/mol}$ is obtained, which is not satisfactory.

Fig. 7 - Log of the rate constant vs. $1/T$.



Discussion

Nowadays it is widely accepted (8,9) that the microstructure of an alloy containing a certain amount of liquid phases is strictly dependent on the value of the dihedral angle 2ϕ . Moreover, it is possible to show (10) that this parameter and the amount of the liquid volume fraction are the relevant parameters defining the mechanical strength of these alloys.

In this paper it has been shown that the kinetics of penetration of the liquid phase into the solid metal, along its grain boundaries, is strongly dependent on temperature, increasing with it.

Previous studies (7) have shown that the dihedral angle of Ni-S and Co-S systems, decreases with increasing temperature, suggesting a well defined relationship between the penetration rate of the liquid sulphide and the angle 2ϕ .

In Fig. 8 it is shown that a nearly linear dependence exists between dY/dt and 2ϕ for the two systems. Only one point in the Ni-S system, corresponding to the lowest temperature, does not fit this linear trend well. The study of penetration process by the method proposed by Mullins leads to the conclusion that the grooving at the solid/liquid interface is governed by volume diffusion. This fact is shown in a quite independent way by the mean value of the exponent of the kinetic laws (three) and by the value of the activation energy ($70 \div 75$ kJ/mol) which is in the range

of typical activation energy values for diffusion in molten salts (11,12). These values are also in very good agreement with that found by Steidel et al. (12) for penetration of liquid Ni-S into a Ni bicrystal.

This fact shows that polycrystalline nickel and cobalt behave in a way which can be quantitatively studied by using model system (e.g. bicrystals), and that the study presented here is accurate enough to interpret the behaviour of practical systems (polycrystalline materials) on the basis of fundamental laws.

In order to reduce the penetrative power of the liquid sulphides, a decrease in the solid/liquid interfacial tension should be provoked, leading to an increase of the dihedral angle ϕ . This could be done in principle, by suitably alloying the base metal or by introducing some other element in the liquid phase. However this last possibility seems to be hardly feasible, in so far as sulphur segregates strongly at the solid/liquid interface (with pure Ni or Co) so that any further decrease in interfacial energy is very difficult to obtain.

Instead, alloying nickel and cobalt with elements able to segregate to the solid/liquid interface and with low affinity for sulphur should represent an efficient way to inhibit grain-boundary penetration.

Conclusions

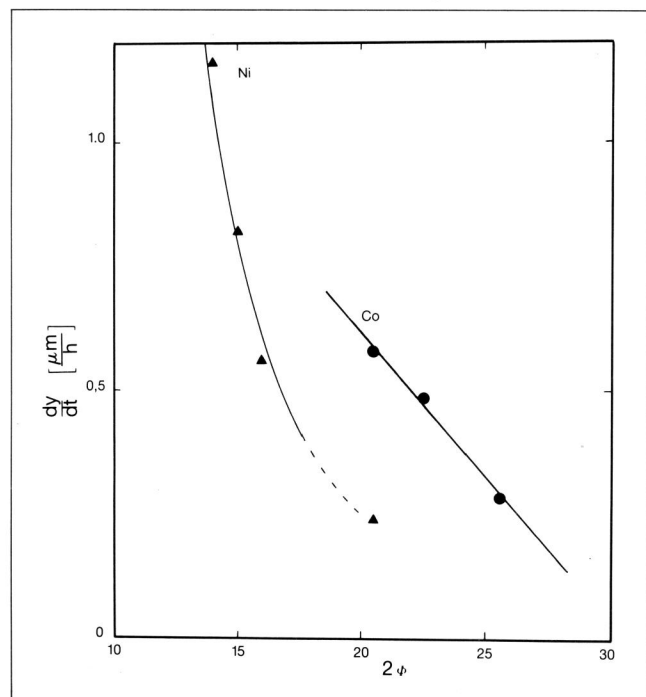
- Nickel and cobalt, submitted to sulphur vapours in the temperature range between 750 and 1100°C, are subject to liquid-phase penetration along grain boundaries.
- The penetration rate increases with the temperature and is inversely proportional to the solid/liquid dihedral angle.
- The kinetic law of the penetration process nearly follows a power of 1/3, showing that the grooving process is governed by volume diffusion;
- The activation energy for the diffusive process is of the order of 70-75 kJ/mol.
- The results obtained, which confront well with those found for nickel bicrystals (12) are important from a technological point of view, because they demonstrate that properties, which are typically orientation dependent, like those related to grain boundaries, can be studied on polycrystalline materials by suitable statistical treatments.

Acknowledgements

This work has been partially funded by "Progetto Finalizzato Metallurgia" of the National Research Council (C.N.R.), Italy.

The authors wish to thank Messrs. C. Candido, P. Vassallo and R. Minisini for their help during this work.

Fig. 8 - Penetration rate as a function of the dihedral angle.



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