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Extrapolating hardness-structure property maps in WC/Co hardmetals

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Abstract

The concept of microstructural design has been extensively used for many years by the hardmetal industry to develop hard and tough products with consistent properties. The primary microstructural features are the size of the hard phase crystals and the volume fractions of the constituent phases. The range of commercial materials now comprises products with grain sizes in the range 0.2–5 μm, but there is interest in manufacturing materials with both finer and coarser structures. The Hall–Petch expression, that predicts high hardness for materials with ever finer grain sizes, underpins this drive. The availability of very fine powders, even down to nanosizes, has stimulated great interest in developing processing routes that can take advantage of these very fine powders. Powders in the nanometer size range are available. The technological challenge is to maintain this small crystal size in the sintered product. The current research has paid careful attention to accurate measurements of hardness and WC grain size, over the whole range of grain sizes, but especially at the finer end, with the objective of reviewing the Hall–Petch predictions for a large population of WC/Co hardmetals with either 6 or 10 wt% Co as binder-phase. Alternative property maps are discussed that may provide a better fit for the experimental data. The use of alternative maps has implications with regard to trends in hardness with grain size and these predictions are discussed. However, they are empirical and currently have no physical basis to underpin their use.

Keywords: Property maps; Hard metals; Hall-petch; Microstructural design

1. Introduction

Size parameters, however defined, exert a strong influence on materials properties. Control of grain size, phase morphology and precipitate volume fraction are three such parameters that allow the materials scientist to design appropriate mechanical and physical properties commensurate with end use, and text books have been written on the physical metallurgy of strengthening methods [1]. In the case of grains it is the constraint on dislocation glide or climb exerted by the boundary that requires external stress to be increased to allow shape changes (yield) to occur. There is a scale effect associated with the physical phenomenon involved (dislocation motion) and a scale effect caused by the constraint mechanism (grain size/boundary). When these scales are dissimilar, in particular when the latter is much greater than the former, then the physical metallurgy of the interaction is reasonably understood and is frequently referred to as Hall–Petch behaviour; i.e. the magnitude of the applied external stress being inversely proportional to the square root of the grain size. However, when the scale parameters approach each other in size the conventional size laws may not apply [2]. It is therefore a popular topic for current research as it is important to identify what boundary conditions apply to the extrapolation of mechanical behaviour to very fine grain sizes. In the case of WC/Co hardmetals this lower boundary lies approximately in the 0.5 μm WC

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grain size range. For grain sizes in the range 0.5–5 μm (measured by the linear intercept method) the Hall–Petch relation describes mechanical behaviour quite well [3] for materials of constant cobalt content.

When the characterisation length becomes similar to the grain size a reduced, or even sometimes inverse, Hall–Petch behaviour becomes apparent. Alternatively flow stress may reach an asymptotic limit [6]. This scale length is in the range 50–100 nm [4,5]. In submicrometer grained hardmetals many WC particles and much of the Co binder phase lies within this size range. Size effects often have a common property, that of exhibiting a maximum at a characteristic value, due to a change in the mechanism of dislocation plasticity [2], and it is important to establish whether this effect will be present in nanometer-sized WC/Co hardmetals.

The Hall–Petch slope is effective in describing mechanical behaviour in the μm to mm range of grain sizes but in a range of engineering materials there is evidence that the slope progressively decreases and asymptotically reaches a plateau in the nanozone. This behaviour can be modelled by an assumption that a work hardened layer is developed close to the grain boundary, and at large grain sizes it is the behaviour in the bulk of the grain that controls the standard Hall–Petch relation, whereas as the grain size decreases the work hardened layer progressively dominates with a different size dependency [7].

The Hall–Petch relation in general predicts that proof strength (i.e. stress, σ, to deform to a given strain, usually 0.1% or 0.2%) should increase with decreasing grain size, d, according to $\sigma = A + Bd^{-1/2}$ where A and B are constants. The equation is semi-empirical but physically based and assumes that a build up of stress in one grain is required before slip is initiated in the adjacent grain. Reasonably detailed mechanical models for hardness and strength have been developed for WC/Co by Gurland and coworkers [8,9] and by the MPI, Stuttgart group [10–13]. The Lee and Gurland model for the dependence of hardness on the properties of the individual constituents of the composite yielded the following expressions:

$$H = H_{\mathrm{WC}} C V_{\mathrm{WC}} + H_{\mathrm{Co}}(1 C V_{\mathrm{WC}}) \quad (1)$$

$$H_{\mathrm{WC}} = 1382 + 23.1\ d_{\mathrm{WC}}^{-1/2} \quad (2)$$

$$H_{\mathrm{Co}} = 304 + 12.7\ d_{\mathrm{Co}}^{-1/2} \quad (3)$$

where H, H_{WC} and H_{Co} are the hardnesses (kgf/mm^2) of the hardmetal, WC and Co phases respectively, V_{WC} is the volume fraction of WC and C is a contiguity factor associated with the WC grain network. The phase sizes (linear intercept) of the WC and Co phases are d_{WC} (mm) and d_{Co} (mm) respectively. Chatfield, however, pointed out [14] that equally good correlation might be obtained by using a series mechanical model in which

$$\frac{1}{H} = \frac{V_{\mathrm{WC}}}{H_{\mathrm{WC}}} + \frac{V_{\mathrm{Co}}}{H_{\mathrm{Co}}} \quad (4)$$

where

$$H_{\mathrm{Co}} = 377 + 1.45\ d_{\mathrm{Co}}^{-1/2} \quad (5)$$

The use of Hall–Petch type equations for modelling changes in hardness with changes in grain size of the WC would seem to be physically reasonable since the process of indentation results in plastic strains of at least 8% and consequently considerable plastic deformation of the WC phase occurs. But it must be noted that Sigl and Exner [10], in their comprehensive analysis of flow mechanisms influencing hardness measurements in WC/Co hardmetals, pointed out that strains ranging from 5% to 20% may be more realistic in relation to hardness indents. They also argued [10] in favour of the Hall–Petch mechanism as a sound explanation for the strengthening associated with finer microstructures. Thus, since the hardness of the individual phases, H_{p}, can be individually related to their physical size by a Hall–Petch type of expression:

$$\text{i.e. } H_{\mathrm{p}} = A_1 + B_1\ d_{\mathrm{p}}^{-1/2} \quad (6)$$

and since the mean phase sizes, d_{p}, are linearly related for constant binder phase content a Hall–Petch expression is not unreasonable for predicting the hardmetal hardness. The validity of Hall–Petch type equations for these two phase materials was examined by the Stuttgart group and found to be reasonably acceptable [10–12]. However, an alternative expression was derived by the University of Witwatersrand group [15] based on a semi-empirical nonlinear function of d_{Co} and d_{WC}

$$H = \alpha_1 + \alpha_2\ d_{\mathrm{WC}}^{\alpha_3}\ d_{\mathrm{Co}}^{\alpha_4} \quad (7)$$

where α_n are constants with values close to 1/4 and $-1/2$ for α_3 and α_4 respectively; these rounded values implying a possible underlying physical cause.

Whatever the modelling approach, with or without extensive plastic deformation of the WC phase, the question of interest is: ‘How well does the Hall–Petch approach work when the phase size of the WC (and hence Co) in the hardmetal is reduced below, or increased above that current in commercial hardmetals?’. For example, the validity of the Hall–Petch equation has been questioned for other materials when grain sizes become very small. Thus, in nanocrystals or very fine grained materials a different form of equation may be required to relate flow stress to grain size, perhaps similar in form to the Hall–Petch equation, but possibly with different exponents for the grain size parameter, such as -1 [16,17]. A more recent approach to incorporating microstructure length scales into constitutive models of mechanical properties, particularly for ceramic reinforced metals [18,19], has been adopted through the use of the concept of strain gradient plasticity where work hardening through interaction of moving dislocations with stored dislocations is dependent on two types of dislocation; those that are called statistically stored