# Hardening of pure metals by high pressure torsion: a physically-based model employing volume averaged defect evolutions

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**Abstract:** A physically-based model to predict the increment of hardness and grain refinement of pure metals due to severe plastic deformation (SPD) by high pressure torsion (HPT) is proposed. The model incorporates volume-averaged thermally activated dislocation annihilation and grain boundary formation. Strengthening is caused by dislocations in the grain and by grain boundaries. The model is tested against a database containing all available reliable data on HPT processed pure metals. It is shown that the model accurately predicts hardening and grain size of the pure metals, irrespective of crystal structure (fcc, bcc and hcp). Also measured dislocation densities show a good correlation with predictions. The influence of stacking fault energy on hardening is very weak (of the order of -0.03 GPa per 100 J/mole).

**Key words**: Severe Plastic Deformation (SPD), dislocations, High-pressure torsion, hardness, grain size

#### 1 Introduction

Severe plastic deformation (SPD) has attracted wide attention as a means of improving properties of metals and alloys, and especially improvements in strength have been targeted [1]. Over 20 years of research in SPD [1,2,3] has revealed that the strength increase of metals due to SPD is strongly dependent on material, with strength increases

in pure Al and Zn being very low (<30 MPa), whilst several pure metals with high melting temperature show very strong increases in yield strength (>500 MPa) [4,5].

In the present work we will focus on high pressure torsion (HPT), which is an SPD method that is particularly effective in terms of the speed at which high deformation can be introduced in materials [6]. The working principle of HPT is depicted in Figure 1 (from [7]). Following extensive work in the field by a range of researchers, extensive data on the hardness and microstructure of HPT processed metals and alloys is now available (e.g. [4,5,6,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22]). Data on hardness increase due to HPT have been published for over 20 pure metals, and several of the factors influencing the hardness of HPT processed pure metals have been investigated in some detail by Edelati and Horita [4,5]. That work has indicated that these hardness values correlate to atomic bond parameters, stacking fault energy, specific heat capacity, specific latent heat of fusion, linear thermal expansion coefficient, activation energy for self-diffusion, melting temperature and shear modulus [5,23,24].

#### Figure 1 The principle of high pressure torsion (HPT) (from [7]).

To fully exploit the capabilities of SPD we need quantitative models that are able to predict the microstructure development during the process and predict resulting mechanical properties based on processing and materials parameters [19,25,26,27,28,29]. In particular, it is important to establish which SPD processed metals possess combinations of properties (for instance strength, density, cost) that are most attractive for application in devises and structures. However, little attention has been given to establishing a model for strengthening and grain refinement that predicts the differences between different metals. In the present work we aim to derive a physically-based model which captures the data on hardness increment and grain refinement of pure metals due to HPT. We will focus our attention on computationally efficient approaches that are based on volume averaged dislocation generation and annihilation, and volume averaged grain boundary creation. This means in practice that we will follow classical approaches to

strengthening (e.g. [30,31,32,33]) and recovery [34]; and include recent insights in the relation between dislocation generation and grain size [19,29]. We aim to show that these can explain published data on material dependence of hardening and grain size for HPT processed pure metals.

# 2 A physically-based model

# 2.1. Overview

To provide a physically-based model for the hardness of HPT processed pure metals we construct a model that takes account of the main aspects of hardening and recovery, focusing particularly those aspects that cause the differences between the various metals.

In a range of publications it has been shown that the strengthening of pure and commercially pure metals due to SPD processing is generally caused by dislocation hardening and grain boundary strengthening (e.g. [19,35,36]). In the present work we will incorporate both strengthening mechanisms.

# 2.2 Dislocation generation and thermally activated dislocation annihilation

To obtain expressions for the total dislocation line length involved in dislocation strengthening and grain size strengthening we proceed as follows. We define  $L_{gen}$  as the total cumulative dislocation linelength generated during the deformation processing. We consider that dislocation are either retained in the grains or subsumed in grain boundaries (existing or new ones) [19,37] or annihilated within the grain [40]. We will consider that the annihilation can be described through a temperature and material dependent annihilation fraction,  $f_{an}$ , i.e.:

$$L_{\rm gb} + L_{\rm ig} = (1 - f_{\rm an}) L_{\rm gen} \tag{1}$$

where  $L_{ig}$  is the total dislocation linelength of dislocations stored in the grain and  $L_{gb}$  is the total dislocation linelength of dislocations that have moved to grain boundaries and have become part of the grain boundary (they are 'subsumed' in the grain boundaries [19,29]). We will consider that the effective width of grain boundaries can be neglected (this is further discussed in section 5) and hence

$$\rho_{ig} = \frac{L_{ig}}{V} \tag{2}$$

where  $\rho_{\rm lg}$  is the (average) dislocation density in the grain, and V is the sample volume. We will here not attempt to model details of the mechanisms of partitioning of dislocations between grain and grain boundary. Instead we will assume that both  $L_{\rm gb}$  and  $L_{\rm ig}$  are effectively proportional to  $(1-f_{\rm an}) L_{\rm gen}$ , i.e. it is assumed that the  $L_{\rm gb}$ :  $L_{\rm ig}$  ratio is in good approximation constant for all the HPT processed pure metals considered. (Consequently,  $f_{\rm an}$  is the dominating factor determining the differences in  $L_{\rm ig}$  between the pure metals, see below.) The influence of this assumption will be further considered in Section 5. Similarly we will not attempt to include twinning or any other deformation induced defect creation in the model, i.e. we assume that if defects other than dislocations or grain boundaries are created, they do not substantially alter predictions. (For discussions on the effect of vacancies see Section 5 and [38,39].)

Dislocation annihilation within grains can occur through several mechanisms. Particularly mutual annihilation of both screw and non-screw dislocations of opposite sign has been evidenced [40]. In the present work we will approximate the rate of dislocation annihilation using the generic exponential relaxation function given by Nes [34]:

$$f_{an} = \exp\left(-t_p / \tau_1\right) \tag{3}$$

where  $t_p$  is the time available for the dislocation annihilation process,  $\tau_1$ , is the time constant of the process. In his work Nes showed that the latter exponential relaxation expression is a good approximation to the expression for network growth due to a range of processes [34].

The main temperature and material dependent factors of this annihilation process can be obtained from the model by Nes [34], which indicates that the time constant of the process,  $\tau_1$ , is of the form

$$\tau_1^{-1} = \frac{C_1}{RT} D_x(T) \exp\left(\frac{\alpha_3 \kappa_2 G b^3}{RT}\right) = \frac{C_1}{RT} D_{x,o} \exp\left(\frac{-E_{A,x} + \alpha_3 \kappa_2 G b^3}{RT}\right)$$
(4)

where  $D_x$  is the self-diffusion constant during the (dynamic) recovery,  $E_{A,x}$  is the activation energy for self-diffusion during the (dynamic) recovery,  $D_{x,o}$  is the preexponential constant for self-diffusion during the (dynamic) recovery,  $\alpha_3$ ,  $\kappa_2$  and  $C_1$ , are constants. Little is known about  $E_{A,x}$  for recovery during HPT. It is expected that  $E_{A,x}$  is substantially lower than the activation energy for self-diffusion due to the presence of a high density of defects, which include dislocations and vacancies [38,39]. In addition, it has been established in several works that the activation energy for self-diffusion generally increases linearly with the melting temperature of metals [41,42]. In this work we will adopt this linear relationship and we will obtain  $E_{A,x}$  by introducing one fittable parameter:

$$E_{\mathrm{A},\mathrm{x}} = C_2 T_{\mathrm{M}} \tag{5}$$

where  $C_2$  is a fittable parameter. (Pressure also influences the activation energy for selfdiffusion [43]. The pressures applied in the HPT processing applied in the data used in this work is similar, and activation volumes are also likely to be similar. Hence differences between the HPT processed metals should not be related to pressure, and this effect is not further considered.)

# 2.3 Sample heating

In the model we will further consider that the sample temperature during HPT deformation can increase due to the work by deformation being converted into heat [44,45]. The temperature increase,  $\Delta T$ , is directly influenced by the ratio of mechanical

deformation energy imposed on the sample divided by the heat capacity, and can be approximated as:

$$\Delta T = \frac{C_3}{\rho C_p} \int \sigma d\varepsilon \tag{6}$$

where  $C_p$  is the heat capacity,  $\rho$  is the mass density,  $\sigma$  is the stress,  $\varepsilon$  is the strain,  $\int \sigma d\varepsilon$ reflects the total mechanical energy of deformation imposed on the sample and  $C_3$  is a constant close to unity. Finite element (FE) model predicting the temperature rise in Al, Cu and Fe during HPT processing is presented in [44,45]. We will show below that the effect of temperature increase during HPT on the hardness after HPT is relatively small, and we will here use an approximation to provide an analytical model. In this approximation we will consider that the total strain imposed on the periphery of the HPT sample on reaching saturation of hardness is about constant (it is about 6 [1]). Additionally we can with very limited loss of accuracy assume that local stress  $\sigma$  has a similar dependency on  $\rho$  for each metal and that the average  $\sigma$  is proportional to  $\Delta$ HV. Following these approximations we can take:

$$\Delta T = C_4 \frac{\Delta HV}{\rho C_p} \tag{7}$$

For Fe processed at 1 turn per minute, it has been shown [44,45] that  $\Delta T$  is 25°C. Using that data we can determine  $C_4$ . The calculated  $\Delta T$  increases nearly linearly with  $G/\rho C_p$  ranging from 0.2°C for Zn to 64°C for Ta.

# 2.4 Strengthening mechanisms: dislocation strengthening and grain boundary strengthening

The increment of critical resolved shear stress due to dislocations,  $\Delta \tau_d$ , is given by [33]:

$$\Delta \tau_d = \alpha_1 G b \sqrt{\rho_{ig}} \tag{8}$$

where  $\alpha_1$  is a constant equalling about 0.3 [33].

In addition to dislocation strengthening also grain size strengthening can occur. It has been shown that at the high strain characteristic for SPD, the total dislocation line length that is subsumed in grain boundaries,  $L_{gb}$ , is in good approximation proportional to the imposed effective strain, which is in turn inversely proportional to the grain size [19,29]. (For further discussion including the effect of average grain boundary misorientation angle see [19,29]). Hence, in good approximation we can take

$$d = C_5 \left[ \exp\left(-t_p / \tau_1\right) \right]^{-1} \tag{9}$$

where *d* is the grain size. The value of  $C_5$  can be determined from the survey of data by Edelati and Horita [23], which shows that in the case of metals with high melting temperature *d*=0.18µm, and hence  $C_5$  should equal 0.18µm. (This means that within the present model *d*=0.18µm can effectively be considered as a saturation for grain refinement in pure metals: decreasing *T* or increasing  $E_A$  will not lead to any further grain refinement.)

Grain boundary strengthening,  $\Delta \sigma_{GB}$ , is mainly determined by *G*, *b*, and the grain size [33,46,47,48]. According to the Hall-Petch relation [30,31,49], it is proportional to  $d^{-1/2}$ , i.e.:

$$\Delta \sigma_{GB} = \frac{k_{HP}}{d_g^{1/2}} \tag{10}$$

with Hall-Petch constant,  $k_{\rm HP}$ . Four main groups of theories and models of the Hall-Petch equation can be identified: the classical pile-up models [50,51,52], those based on dislocation interactions [33,53,54], the grain boundary source theories [55] and, more recently, strain gradient crystal theories, which include aspects of the other three in a computationally demanding framework [56,57]. However, no clear experimental evidence has been able to support the exclusive validity of any of these models [56] for all metals. We will not consider grain boundary strengthening mechanisms in detail, instead we will use that according these theories in general  $k_{\rm HP}$  is proportional to  $Gb^{1/2}$  (see e.g. [33,58]). We will obtain  $k_{\rm HP}$  using data on  $k_{\rm HP}$  for one metal (Ni) on which reliable and consistent data is available (both [59] and [60] independently provide  $k_{\rm HP}$ (Ni)

= 180 GPa. $\mu$ m<sup>-1/2</sup>) and data on *G* and *b*. (This simplifying assumption may introduce some level of inaccuracy in the strengthening prediction. This is further discussed in Section 5.)

In the theories described above, the basic mechanism behind grain boundary strengthening is grain boundaries increasing the build-up of dislocations [61]. Hence the appropriate superposition rule for  $\Delta \sigma_{GB}$  and  $\Delta \tau_d$  here is a quadratic one [62,63,64,65], e.g.:

$$(\Delta\sigma)^2 = (\Delta\sigma_{GB})^2 + (M\Delta\tau_d)^2 \tag{11}$$

(For further discussion of superposition rules, see Section 5.4.)

#### 3 Data

# 3.1 Hardness data of HPT processed metals

The Vickers hardness at the saturated level (HV) of a wide range of pure metals and semi-metals with various crystal structures processed through severe plastic deformation (SPD) have been reported [4-22,28,66]. In this work, we study the increment of hardness ( $\Delta$ HV) of 17 high purity (better than 99.9%) elements due to HPT reported in [4,5,9,10,23,28,66] (see Table 1).. In these studies sample were cut to discs 10 mm in diameter and 0.8 mm thick, under a selected pressure in the range *P* = 1–6 GPa for up to 15 rotations. The 17 metals selected for the present modelling study, were arrived at by initially considering all metallic elements for which post HPT hardness data is available in [28], and deleting all elements for which only data for processing at elevated temperature (>300°C) is available (Mo, W and Re) and metals which show a hardness decrease during HPT. All hardness data was obtained from the work by Edelati and Horita [4,5,66].

The increment of hardness ( $\Delta$ HV) after SPD is obtained by subtracting the hardness at annealed state (HVi) from the hardness at the saturated level (HVs). It would have been desirable to quantify all the data under identical experiment condition, however, no

systematic database on Vickers hardness data of the elements at annealed state before SPD (HVi) is available. We have performed exhaustive database searches as well as investigating the references in the present work which contain HVi data [4,5,23]. (Many online databases take data from [67]). These HVi data reflect various conditions including: ill defined 'as-received' or annealed, and we use the smallest reported value one for each element which is closer to the true level of pure un-deformed metal (Table 1). In the present work most data are adopted from the same source [67].

#### 3.2 Grain size of HPT processed metals

Grain size data was obtained from the survey in [68].

	G	$T_{\sf m}$	b	$C_{ m p}$	HVi	∆HV measured	$\Delta T$ model	$\Delta \sigma_{GB}$ model	homodel	∆HV model	grain size model
	GPa	К	nm	J/kg.K	GPa	GPa	К	MPa	$10^{14} \text{ m}^2$	GPa	μm
Mg	17.7	922	0.3197	1020	0.29	0.057	0	38	1.4	0.17	1.17
AI	27.1	933	0.2864	900	0.167	0.15	1	58	1.6	0.25	1.17
Ti	40.1	1933	0.2896	520	0.97	1.63	10	197	27.9	1.56	0.22
V	47.4	2163	0.2618	490	0.63	1.73	15	243	33.3	1.82	0.20
Cr	119	2133	0.2498	450	1.06	3.70	36	572	26.9	3.93	0.23
Fe	83.1	1803	0.2482	440	0.61	2.41	25	376	21.6	2.44	0.26
Co	77.9	1763	0.2506	420	1.04	2.50	26	347	20.3	2.24	0.27
Ni	76.5	1723	0.2492	440	0.64	2.38	25	336	19.4	2.14	0.27
Cu	46	1353	0.2556	380	0.37	0.93	12	171	10.6	0.97	0.38
Zn	37.9	693	0.2665	390	0.35	0.009	0	35	0.2	0.11	6.24
Zr	34.8	2123	0.3179	270	0.90	1.63	14	176	30.2	1.55	0.21
Nb	38.2	2743	0.2864	260	0.35	2.00	20	204	37.8	1.71	0.19
Pd	52.1	1823	0.2751	240	0.46	1.67	28	239	21.9	1.71	0.25
Ag	29.2	1235	0.2889	235	0.25	0.69	8	98	7.0	0.57	0.47
Та	70	3273	0.2856	140	0.87	3.26	70	374	37.8	3.13	0.19
Pt	62.2	2043	0.2775	130	0.55	1.98	56	289	22.9	2.10	0.24
Au	28.1	1333	0.2884	128	0.216	0.59	17	102	9.2	0.63	0.40

Table 1Experimental data on hardness increment due to HPT processing,  $\Delta$ HV, and hardness<br/>of pure undeformed metal, HV<sub>o</sub>. See text for source of data. Also displayed are<br/>predictions of  $\Delta \sigma_{GB}$ ,  $\rho$ ,  $\Delta$ HV,  $\Delta T$  and the grain size with the present model (see text).<br/>Comparisons of measured and predicted  $\rho$ ,  $\Delta$ HV and grain size are plotted in Figures<br/>2, 3 and 5.

# 3.3 Physical data

Data for shear modulus, *G*, Burger's vector, *b*, mass density and heat capacity,  $C_p$ , (in Table 1) were obtained from CES Edupack 2011 [69].

# 4 Model calibration and modelling results

We applied the above model to hardness and grain size data on the 17 pure metals by calibrating the 4 parameters  $L_{gen}$ ,  $C_1$ ,  $C_2$ ,  $C_6$  (= $\alpha_3 \kappa_2$ ). (One iterative step is required, where  $\Delta$ HV is needed to calculate  $\Delta T$  using Eq. 7. This is readily solved by first setting  $\Delta T$ =0 and optimizing the 4 parameters, and then using the calculated  $\Delta$ HV in a next iteration.) Several ways of fitting have been tested, all with very similar results. We will here report the method that demonstrates most clearly the predictive capability of the present model. We select the 4 data that are considered the most reliable based on a 4 criteria: availability of multiple measurements from different groups, low variability in measured values, good availability of the high purity metals involved (reducing potential for slippage and microcracking influencing results). The 4 data selected are  $\Delta$ HV for Al, Cu and Ni and the grain size for HPT Cu.

The resulting model fit captures all the main variations (see Figure 2) and the RMSE for  $\Delta$ HV for 17 elements is 0.14 GPa, which is 9% of the measured hardness averaged for the metallic elements. This remaining error is considered to be consistent with the measurement accuracy. The average prediction accuracy of grain size for 15 metallic elements is 15% (see Figure 3). Figure 4 presents the measured and predicted  $\Delta$ HV as a function of the temperature. Also plotted is the predicted ratio of grain boundary strengthening to dislocation strengthening.

Figure 2  $\Delta$ HV predicted by the physically-based model compared with experimentally measured  $\Delta$ HV. Data for 17 pure metals. See text for source of experimental data.

Figure 3 Grain size predicted by the physically-based model compared with experimentally measured grain size. Data for pure metals. See text for source of experimental data.

#### 5. Discussion

# 5.1 Verifying the model

The previous section shows that the model provides a very good accuracy for the database with hardness and grain sizes of pure metals; and that is achieved by using 4 fittable parameters. This represents good evidence that the model is accurate and that the physical basis of the model, even though it may ignore some secondary effects, is essentially sound. To provide additional confidence in the physical basis of the model we will critically consider the various predictions on microstructure and dislocation annihilation kinetics. We will consider in more detail predictions of  $\rho_{ig}$ ,  $E_{A,x}$ ,  $\tau_i$ , which are the parameters most amenable to experimental assessment or comparison with available data.

The physically-based model predicts grain sizes ranging from 0.18  $\mu$ m for Nb and Ta to 9  $\mu$ m for Zn. In Figure 5 the predicted and measured grain sizes are plotted as a function of the homologous temperature. The average variation in the experimental data (where 2 values for grain size after HPT) are available is 27%. Hence the accuracy of the predictions (15%) is fully consistent with the accuracy in the measured data.

The physically-based model predicts dislocation densities ranging from  $2 \times 10^{12}$  m<sup>-2</sup> (for Zn) to  $3 \times 10^{15}$  m<sup>-2</sup> (for Nb and V). Data on dislocation densities in pure metals deformed by HPT or ECAP are available for Al, Ni, Cu, Ag, Au and Nb. We obtained published data on measured dislocation densities in these pure metals [35,38,70,71,72,73,74,75,76,77]<sup>\*</sup>. In Figure 6 the predicted dislocation densities from the

<sup>&</sup>lt;sup>\*</sup> If no literature data on dislocation densities in HPT processed pure metal is available, data on dislocation density obtained for ECAP processed samples at a number of passes leading to the peak in hardness was used. The obtained data was cleaned by the following procedure. If dislocation densities for one metal reported in multiple publications differ by factor of more than 4, and one of these data points is inconsistent

present model are compared with published data on measured dislocation densities. Averaged reported experimental dislocation densities generally correspond within a factor 2 with predicted ones. Considering that reported measured dislocation densities of nominally identical materials can sometimes differ by a factor 2 to 3, the level of correspondence shown in Figure 6 is considered consistent with the model. The present predicted averaged dislocation densities in grains are also broadly consistent with the predicted maximum dislocation densities for pure metals based on models incorporating the assessment of annihilation of individual dislocation of different character (screw and non-screw) [40].

The predicted low dislocation density for Zn is consistent with Differential Scanning Calorimetry studies on Zn deformed at 77K which show that on linear heating the dislocation annihilation rate is substantial at room temperature [78]: clearly dislocation annihilation in Zn during SPD at room temperature will be very rapid.

The highest value of  $E_{A,x}$  obtained through fitting is 19 kJ/mole for Ta. This activation energy is substantially lower than the activation energy for self-diffusion in undeformed Ta and also for other metals  $E_{A,x}$  is substantially lower than the activation energy for selfdiffusion in the corresponding undeformed metal. Within our model this means that the extensive amounts of defects introduced in the severe plastic deformation (dislocations, vacancies [40,38,39]) drastically reduce energy barriers for self-diffusion. The present activation energies are close to the range of activation energies found for radiation enhanced diffusion (for instance it is 36 kJ/mole for ion-beam-enhanced diffusion of Au in amorphous Si [79]) and diffusion in multilayer structures (20 kJ/mole for Ni diffusion into Ti in Ni-Ti multilayers [80]), both of which are characterized by high densities of defects. The activation energies for boundary diffusion in Ta and V determined from grain growth experiments on Ta and V produced by electron-beam evaporation and magnetron sputtering deposition have been reported as 30 and 20 kJ/mol [81], whilst binding energies for di-vacancies in metals is typically in the range 10 to 20 kJ/mol. It is thus surmised that the thermally activated annihilation of dislocations during HPT is

with the dislocation hardening equation (Eq. 1) by over predicting measured strength/hardness by more than a factor 2, then that data point is deleted.

strongly influenced and aided by a high density of deformation induced defects such as vacancies and dislocations [38,39,82].

The model indicates that decreasing process time (e.g. increasing rotation rate) during HPT increases hardness. For an AZ31 Mg alloy, experiments have confirmed this [83]. The model indicates that increasing the process temperature decreases the hardening. For a 2024 Al alloy, experiments have confirmed this [84]. (It should be mentioned that in this alloy also precipitation hardening occurs, which provides an additional temperature dependent effect.) The model indicates that decreasing the process temperature increases the dislocation density. For a 2024 Al alloy processed at -196°C and room temperature, TEM experiments have confirmed this relation [84].

Hard to deform high purity metals Mo and W can be HPT processed to obtain hardness values close to 1 GPA, however HPT processing needs to be conducted at elevated temperature, i.e. with heated anvils [85]. In this case the sample temperature during dislocation annealing is difficult to obtain. The present model can predict grain size and hardness of Mo and W processed at elevated temperature well provided that the effective temperature for the dislocation annihilation is taken as the average of anvil preheat temperature and room temperature.

- Figure 4 Measured and predicted  $\Delta HV$  as a function of the temperature. Also plotted is the predicted ratio of grain boundary strengthening and dislocation strengthening. Data for 17 pure metals. See text for source of experimental data.
- Figure 5 Measured and predicted grain size as a function of the homologous temperature. Also plotted is the predicted ratio of grain boundary strengthening and dislocation strengthening. Data for pure metals. See text for source of experimental data.
- Figure 6 Measured dislocation densities for SPD processed pure metals compared with prediction from the present model. See text for source of experimental data.

# 5.2 Data accuracy

To better understand the influence of data accuracy on the present model assessment we considered the accuracy of data on the main parameters in the model, i.e. G and  $T_{\rm m}$ .

Data on *G* of pure metals gathered from 4 handbooks and 4 Internet database, which span a period of decades, are generally inconsistent. (This is not uncommon, data on physical and chemical properties of several elements are inconsistent between different data sources, see e.g. [86].) The largest spread in reported values of *G* for pure metals occurs for Hf and this metal was removed from consideration in the present study. Further also Zn and Pd show significant variations (5 to 10%) in reported *G*. The impact of these variations was checked by inserting different reported *G* values, and it was found that the model accuracy is not significantly influenced. To understand the reasons behind the inconsistencies, we have to trace back to the original articles on experimental measurements of the shear moduli concerned. One issue that can be identified is that some data on *G* derives from measurements on single crystals. The shear modulus of polycrystalline materials can be derived from elastic constants of the single crystal, but the relation between elastic constants and shear modulus is not unique [44]. Two widely used averaging methods are the Voigt-Reuss-Hill [87,88,89] and Hershey-Kroner-Eshelby method [90,91]. These issues are further investigated elsewhere [92].

The melting temperature of all metals is known to a high accuracy.  $T_{\rm m}$  of Al, Co, Ni, Cu, Zn, Nb, Pd, Ag, Pt and Au is a defining fixed temperature of the International Temperature Scale of 1990 (ITS-90). 26 sources including 6 Internet databases and 17 Handbooks with multiple tables have also been checked for the other 8 elements (Mg, Ti, V, Cr, Fe, Zr, Hf and Ta); they are all in good agreement with variations typically smaller than 2%.

It is noted that the purity and testing atmosphere can cause variation of mechanical prosperities in nominally "pure" metals [43]. The data used in the present study is all for high purity metals and hence it is thought that these factors do not play a role in the present study.

#### 5.3 Other correlations and adaptive models

In parallel with the present study we conducted an adaptive numerical modelling (ANN) (see e.g. [86,93,94]) study of the  $\Delta$ HV data, using as inputs 13 physical, chemical and mechanical parameters of pure metals, including the parameter that have recently been reported to show a correlation with HV of HPT processed pure metals [4,5,23,24]. Details of this ANN work are reported elsewhere [92]. The ANN assessment shows results that support the present physically-based model. In particular it identifies the shear modulus and melting temperature as being the main parameters influencing the hardness, with none of the other parameters having a statistically significant influence. As can be expected, the accuracy of the ANN model is almost the same as the physically-based model.

It should be noted that some of the physical, chemical and mechanical parameters of metallic elements have strong correlations with the melting temperature, particularly heat of fusion, cohesive energy and thermal expansion coefficient show a strong correlation (correlation coefficients >0.9). This means that these parameters in themselves will show a correlation with  $\Delta$ HV or  $\Delta$ HV/*G* when plotted. However, both the ANN investigation [92] and the present model show that the data does not support any suggestion that there is a causal relation. The present physically-based model then indicates that the activation energy for a relaxation process (here considered to be dislocation network growth), which correlates to the melting temperature, is the main material-dependent parameter of the underlying process.

We further investigated whether stacking fault energy (SFE) has a correlation with the  $\Delta$ HV data by determining the correlation between the residual error after application of the physically-based model and reported stacking fault energies of pure metals (using SFE data for 10 pure elements collated in [23], ranging from 16 for Ag to 240 for Zr mJ/m<sup>2</sup>). This analysis shows that there is a very weak correlation between SFE and the residual error in  $\Delta$ HV (correlation coefficient -0.3), with a linear fit suggesting a weak effect: the slope of a plot of residual error in  $\Delta$ HV vs. SFE is -0.03 GPa per 100 kJ/mol. As expected the negative slope indicates enhanced softening/recovery with increasing SFE. However, it should be stressed that the effect is very weak; it accounts for less than

2% of experimentally observed variation in  $\Delta$ HV between the pure metals, which is smaller than the expected experimental reproducibility. (Also if the residual errors are normalised by *G* correlation with SFE is very weak.)

# 5.4 Alternative models and mechanisms

As indicated in the introduction, the aim of the present work is to show that hardening of pure metals can be explained and predicted based on a model incorporating volume averaged dislocation generation and annihilation, and volume averaged grain boundary creation. Comparison with the available data shows that the present model has been successful in achieving this. It is evident that for a full model of all processes involved, further model refinement would be needed. Nevertheless the present model is valuable because it reveals the relative importance of the basic mechanisms (annihilation, grain refinement, dislocation hardening) to strengthening due to SPD.

Partly as a result of the volume averaged approach, the present model makes a number of choices that appear to deviate from other models and analyses. For instance, the width of the grain boundary is taken to be negligible and only two destinations for dislocations are considered: a generic 'subsumed in grain boundary'  $(L_{gb})$ , which does not distinguish between low and high angle grain boundaries and 'in grain'  $(L_{ig})$ . This should be considered as a simplification of more detailed assessments of dislocation structure which can identify dislocations i) subsumed in equilibrium high angle grain boundaries, ii) close to a grain boundary, forming a non-equilibrium boundary, iii) in low angle grain boundaries, iv) in cell walls and v) residing in the grain away from the boundaries/walls. The present model should not be taken as evidence against this complexity, rather the model should be taken as an indication that even though this range of complex structures exists, modelling of strengthening and grain size can be successfully achieved based on just two states ('subsumed in grain boundary' and 'in grain'). The challenge for future assessment will be to clarify how this complex range of states maps onto the simplified two-state model, and on identifying whether 3 state and 4 state models can achieve similar or better model results.

Although grain refinement is often mentioned as being the main factor in strengthening of SPD processed metals, several more detailed analyses that incorporate strengthening models and dislocation density measurements have indicated that dislocation hardening is the main factor determining the strengthening of many SPD processed pure and commercially pure metals [19,35, 72,95,96]. The present model, and particularly Figure 4, indicates that dislocation hardening is indeed the main strengthening mechanism for pure metals. (The possible exception might be very low melting point metals such as Zn, where dislocation annihilation is nearly complete, and accurate measurement of hardening is not possible.) There is also a strong correlation between grain size and  $\Delta$ HV/*G* (see Figure 7). However, this is predominantly an indirect, non-causal relation: both grain refinement and the main strengthening effect (dislocation strengthening) depend strongly on dislocation annihilation.

One may consider that, even though it would appear to be inconsistent with the classical interpretations of Hall-Petch hardening, a linear superposition rule for the superposition of grain boundary strengthening and dislocation strengthening may be appropriate. This would modify Eq. 11. This model modification was checked and the main findings are that, after reoptimising of parameters:

- the model accuracy reduces somewhat to a RMSE for  $\Delta$ HV of 0.16 GPa (0.14 GPa in the model with quadratic superposition),

- the predicted ratio of grain boundary strengthening to dislocation strengthening changes: it reduces by a factor that is on average 0.7,

- the prediction of dislocation density is very similar,
- the prediction of grain size nearly identical.

In our opinion this linear superposition is inconsistent with basic strengthening theory, but even if that was ignored and linear superposition is adopted, the above findings show that the influence on the present findings is very limited.

It is noted that the present treatment of thermally activated dislocation annihilation using a single activation energy for each element is likely to be a simplification, as the rate of dislocation annihilation is likely to be influenced by multiple interacting thermally activated processes, e.g. vacancy generation following annihilation of dislocations [40], vacancy annihilation, vacancy diffusion, dislocation network growth, self-diffusion. Future attempts at modelling process temperature dependence of the hardening would therefore need to consider multiple thermally activated processes. In refinements of the model also a detailed modelling of vacancy concentration and it effect on strength (see eg [39,97]) and dislocation annihilation should be considered.

#### 6 Conclusions

A physically-based model to predict the increment of hardness and grain refinement of pure metals due to severe plastic deformation (SPD) by high pressure torsion (HPT) is proposed. The main factors included in the model are:

- volume-averaged thermally activated dislocation annihilation, which leads to a prediction of the total dislocation linelength of dislocations stored in the grain,  $L_{ig}$ , and the total dislocation linelength of dislocations that are subsumed in the grain boundaries,  $L_{gb}$ ;

- volume-averaged grain boundary formation;

- activation energy for dislocation annihilation which is proportional to the melting temperature;

. strengthening due to grain boundaries, which is obtained using the classical Hall-Petch type expression, and strengthening by dislocations.

The model is tested against a database containing all available reliable published data on HPT processed pure metals. It is found that even though the model only considers volume averaged evolution, it accurately predicts hardening and grain size of the pure metals, irrespective of crystal structure (fcc, bcc or hcp). Also measured dislocation densities show a good correlation with predictions. Further analysis based on the present model indicated that the influence of stacking fault energy on hardening is very weak. Heat of fusion, cohesive energy and thermal expansion coefficient of the metals show a strong correlation with the melting temperature and hence also show a correlation with the hardness increase. However the present model indicates there is no evidence that this is a causal relation.

Figure 7 Plot showing the correlation between  $\Delta HV/G$  and 1/d. In the model the correlation is an indirect, mostly non-causal one. See text for source of experimental data.



Figure 1 The principle of high pressure torsion (HPT) (from [7]).



Figure 2  $\Delta$ HV predicted by the physically based model compared with experimentally measured  $\Delta$ HV. Data for 17 pure metals. See text for source of experimental data.



Figure 3 Grain size predicted by the physically based model compared with experimentally measured grain size. Data for pure metals. See text for source of experimental data.



Figure 4 Measured and predicted  $\Delta HV$  as a function of the temperature. Also plotted is the predicted ratio of grain boundary strengthening and dislocation strengthening. Data for 17 pure metals. See text for source of experimental data.



Figure 5 Measured and predicted grain size as a function of the homologous temperature. Also plotted is the predicted ratio of grain boundary strengthening and dislocation strengthening. Data for pure metals. See text for source of experimental data.



Figure 6 Measured dislocation densities for SPD processed pure metals compared with prediction from the present model. See text for source of experimental data.



Figure 7 Plot showing the correlation between  $\Delta HV/G$  and 1/d. In the model the correlation is an indirect, mostly non-causal one. See text for source of experimental data.

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