

7 Influence of the Residual Chemical Composition on the Dynamically Recrystallized Grain Size of Fire-Refined 99.9% Pure Coppers

7.1 Improvement of Mechanical Properties by Grain Refinement

The mechanical properties at room temperature of an annealed 99.9% pure copper will depend on the initial grain size and texture, but not as much on the residual composition. As is known a finer initial grain size will improve mechanical properties in general. A strong texture produces a weighted mechanical response [1]. Commonly the properties of copper are improved by grain refinement and by avoiding strong textures. This work addresses grain refinement produced by dynamic recrystallization. Other grain refinement techniques include: small additions (as little as 0.10%) of Li, Bi, Pb or Fe during the melt [2, 3], rapid cooling or mechanical vibration during casting [4] and grain refinement through static recrystallization [5, 6, 7, 8, 9]. Final products made of commercial purity coppers employ a combination of dynamic recrystallization and static recrystallization to refine the microstructure [10]. A characteristic of dynamically recrystallized grains is that the texture components of the processed microstructure tend to be weak, unlike refinement by cold working and annealing. If various grain sizes of comparable texture [11] are tested at room temperature then a Hall-Petch relationship of the form

$$\sigma(\varepsilon) = \sigma_{HP}(\varepsilon) + K_{HP}(\varepsilon) \cdot D_0^{-1/2} \quad (7.1)$$

can be constructed where $\sigma_{HP}(\varepsilon)$ and $K_{HP}(\varepsilon)$ are constants at a particular strain and, D_0 is the initial grain size. As usual σ and ε represent the stress and strain respectively. The Hall-Petch relationship describes the increase of yield stress as the initial grain size diminishes, however on eq. 7.1, which specifies stress-strain values, only strains up to about 0.2 should be used. Figure 7.1 and table 7.1 by Hansen and Ralph [12] show the behavior of eq. 7.1 in tension after selecting copper samples of comparable texture. This work will instead discuss the relationships that describe the hot working conditions necessary to produce a dynamically recrystallized grain size as an attempt to improve the microstructure of fire-refined 99.9% pure coppers.

The effect of initial grain size during strain hardening at room temperature extends beyond the description given by a Hall-Petch relationship. Kok et al. [13] reviewed the room temperature copper data of five other research teams and based on the MTS model proposed a two state variable hybrid model. Kok et al. proposed that grain size not only enters the initial yield but also continues to enhance hardening with increasing strain. Figure 7.2 illustrates the argument of Kok et al. where a smaller grain size certainly affects the initial yield, but after additional strain the hardening difference also increases, as a smaller A than B would suggest. Formability (malleability and ductility) also improves by grain refinement, as higher strains are possible without failure of the material. In 99.9% pure copper elongations of over 50% have been reported on highly refined microstructure [14, 15]. A link between the optimal hot working conditions to produce a desired dynamically recrystallized grain size and the expected room temperature mechanical properties of 99.9% pure copper is here presented.

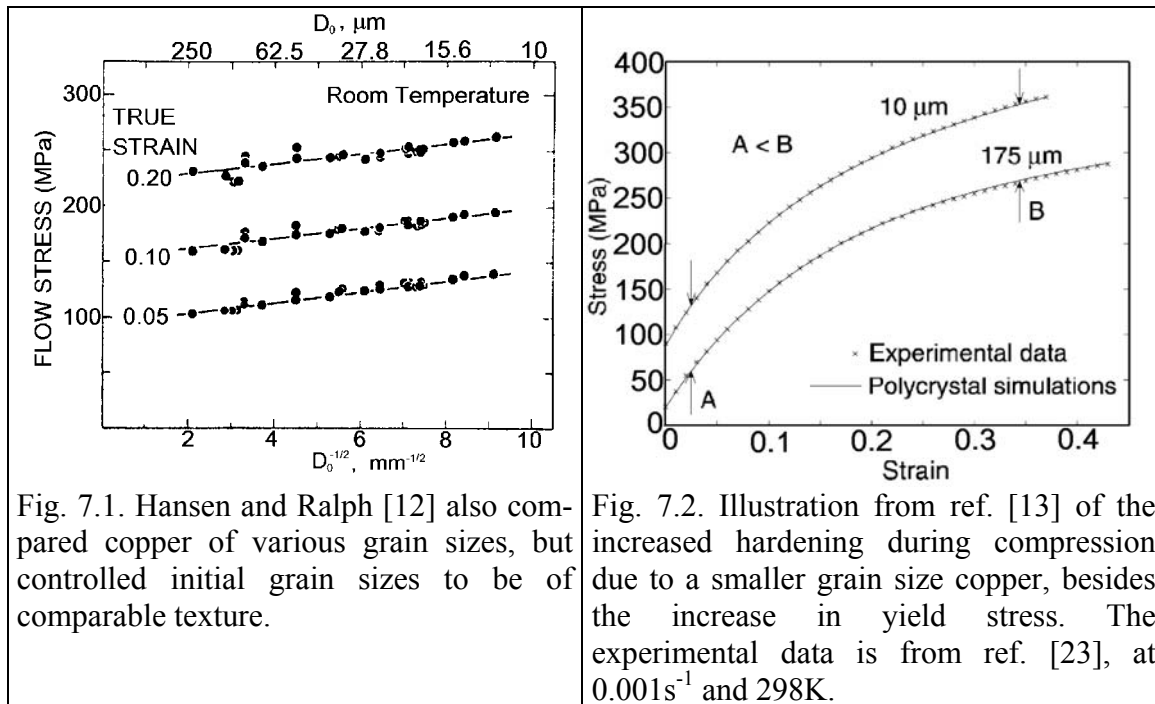


Fig. 7.1. Hansen and Ralph [12] also compared copper of various grain sizes, but controlled initial grain sizes to be of comparable texture.

Fig. 7.2. Illustration from ref. [13] of the increased hardening during compression due to a smaller grain size copper, besides the increase in yield stress. The experimental data is from ref. [23], at 0.001s^{-1} and 298K.

Table 7.1 Constants in the Hall-Petch eq. 7.1 from tensile tests data [12] in fig. 7.1.

True Strain (ϵ)	$\sigma_{HP}(\epsilon)$ in MPa at 20°C	$K_{HP}(\epsilon)$ in $\text{N/mm}^{3/2}$ at 20°C
0.05	95	5.0
0.10	154	4.6
0.20	222	4.5

7.2 Influence of Cu_2O Precipitates on the End Microstructure

Earlier on this work the observation had been made that copper B produced a finer dynamically recrystallized grain size and that copper A produced the coarsest grain, particularly at temperatures above 850°C (see ref. [16] or fig. 3.46 of the results chapter of this work). The point was made that the residual composition of Pb, Ni and, Ag could be adopting a more prominent role than the effect of oxygen at temperatures above 850°C, however more research is needed. A finer dynamically recrystallized grain size was observed as the levels of Pb, Ni and, Ag increased. Pb is immiscible in Cu and has been observed to form part of small inclusions ($0.3\mu\text{m}$ - $3.59\mu\text{m}$). The immiscible particles could be promoting nucleation during high Zener-Hollomon parameter values, by creating more annealing twin boundaries, which then lose coherency to form a new grain [17]. Ni and Ag form solid solutions in Cu, but no effect on the grain size has been reported at the low content levels as the ones found in these fire-refined coppers. The residual content of Pb, Ni and Ag during DRX above 850°C may be more decisive than the oxygen content, unfortunately the dynamically recrystallized grain sizes produced above 850°C are considered large and the room temperature mechanical properties vary little with large grain sizes.

The number of different residual elements in fire-refined copper allows for much speculation about which element is truly responsible for the differences in dynamically recrystallized grain sizes, however this work has provided information to propose educated assumptions. Another deduction that can be made comes by first analyzing

only the residual composition of coppers A and B (see the residual chemical composition tables 2.1, 2.2, 2.3 on the procedure chapter). One can suppose little difference in the elements that do not form a second phase with copper, including P (297ppm for Cu A and 253ppm for Cu B). Then by observing fig. 3.46 at temperatures above 850°C a finer grain size is noticed when the oxygen level is higher. If the coppers with higher oxygen level (Cu C and then Cu B) are now analyzed on fig. 3.46 and acknowledging that Cu C has 100ppm less of P than the other two coppers then a coarser grain size is observed. The most abundant residual element, P, seems to promote a somewhat finer dynamically recrystallized grain size at higher temperatures as the content level increases.

The residual oxygen has been reported [18, 19] to promote a finer dynamically recrystallized grain size among purer coppers (99.999% to 99.9% pure), however among fire-refined 99.9% pure coppers the effect seems to be the same below 850°C. At lower compression temperatures where precipitation of Cu_2O particles has increased then the volume fractions present are enough to control the grain growth if the strain rates are in the range of this study. On the other hand at higher temperatures the results on static grain growth on fig. 3.51 show that after enough time the migrating borders of the copper with higher oxygen become unpinned and grow faster, however the strain rates used during the compression tests were much faster and unpinning was not allowed. At temperatures above 850°C oxygen promoted a slightly finer grain size among fire-refined 99.9% pure coppers, whereas at lower temperatures the variation of oxygen, here investigated, did not promote noticeable grain size differences.

7.3 Prediction of the Dynamically Recrystallized Grain Size

One of the utmost important objectives of this work is to predict the dynamically recrystallized grain sizes, because of the consequences grain size has when copper is worked at room temperature. Physically based, semi-empirical and empirical relationships exist that have helped predict with various levels of reliability the dynamically recrystallized grain size. The physically derived Derby relationship [20],

$$\frac{\sigma_{ss}}{\mu(T)} \left(\frac{D_{rex}}{b} \right)^{n_{Derby}} = K_{Derby} \quad (7.1)$$

for pure metals was applied to predict the dynamically recrystallized grain diameter, D_{rex} . Expression 7.1 relates the registered steady state stress, σ_{ss} , during compression and the produced dynamically recrystallized grain diameter. On the latter relationship $\mu(T)$ is the shear modulus, which normalizes the registered steady state stress and b is the Burgers vector, which normalizes D_{rex} . Figure 7.3 plots the relationship using the three coppers and table 7.2 resumes the values of n_{Derby} and K_{Derby} . The exponent n_{Derby} had been theorized by Derby to be 2/3 and the constant K_{Derby} to lie between 1 and 10 if used to model pure metals. The n_{Derby} exponent and K_{Derby} constant on the Derby relationship were increasingly higher for the copper that produced a finer grain size, i. e. Cu B produced the finest and Cu A the coarsest grain size. Gao et al. [19] found a constant slope of 0.75 ± 0.05 regardless of the purity level, however here slopes of 0.72, 0.94 and 0.85 were found for coppers A, B and C respectively. Derby's relationship

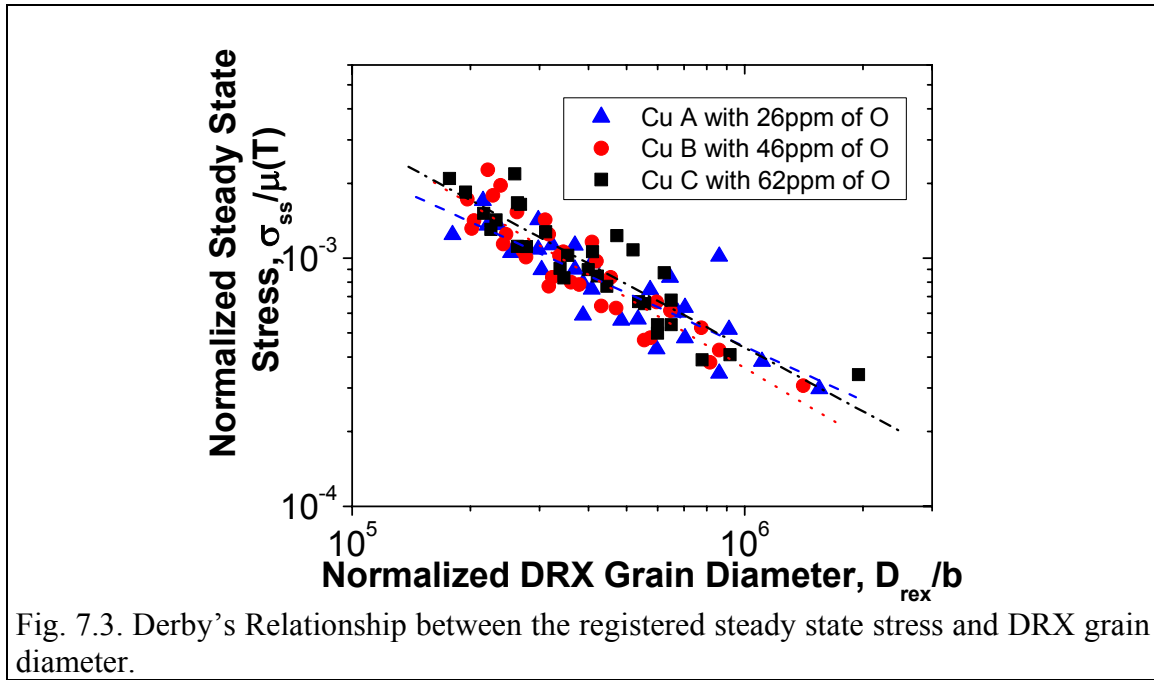


Fig. 7.3. Derby's Relationship between the registered steady state stress and DRX grain diameter.

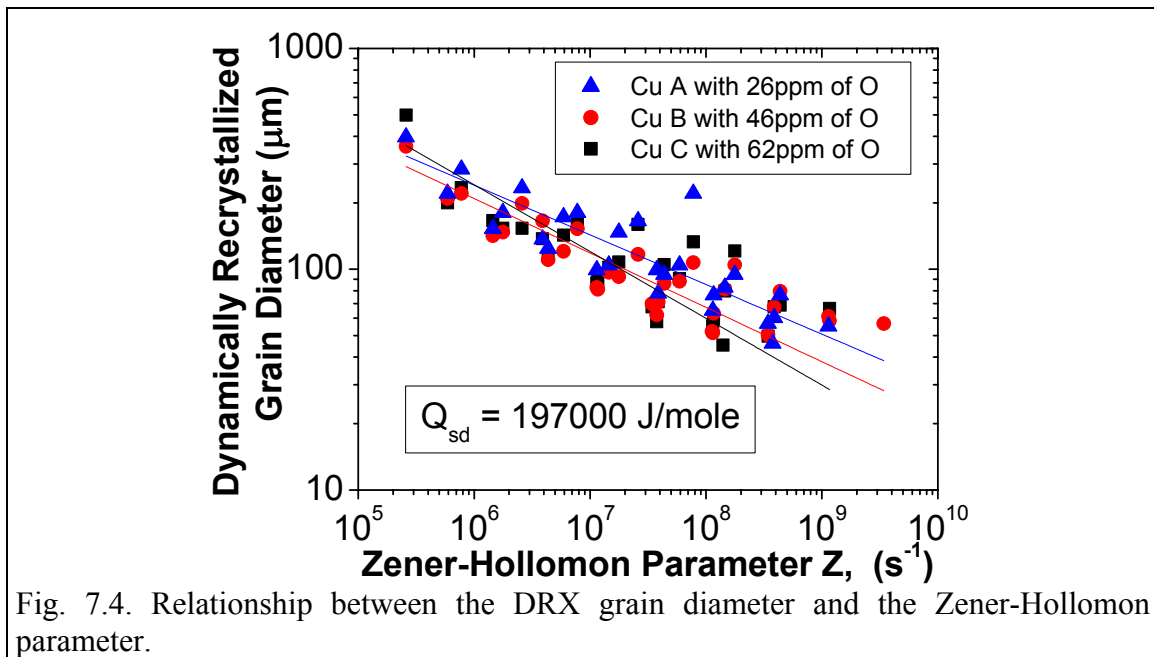


Fig. 7.4. Relationship between the DRX grain diameter and the Zener-Hollomon parameter.

Table 7.2 Constant values in the relationships that describe the DRX grain diameter.

	Copper A	Copper B	Copper C
K_{Derby} of eq. 7.1	9.1	166.4	55.7
n_{Derby} of eq. 7.1	0.72	0.94	0.85
K_{rex} of eq. 7.2	5385.7	6281.8	15811.9
n_{rex} of eq. 7.2	0.225	0.246	0.303
R^2 using eq. 7.1	0.718	0.833	0.813
R^2 using eq. 7.2	0.740	0.817	0.731

normalizes the data of this precipitation-hardened copper, however not much better (see R^2 on table 7.2) than the semi-empirical D_{rex} - Z relationship

$$D_{rex} = K_{rex} Z^{-n_{rex}} \quad (7.2)$$

where Z is the Zener-Hollomon parameter ($Z = \dot{\epsilon} \exp(Q_{sd}/RT)$). Despite the lack of a formal physical demonstration eq. 7.2 invokes a physical justification by using the self-diffusion activation energy, Q_{sd} . On eq. 7.2 the constant K_{rex} and exponent n_{rex} increased as the oxygen level increased, but the dispersion of data was noticeable (see fig. 7.4). In the future, the common terms on relationships 4.2, 4.4, 7.1 and, 7.2 may help predict the dynamically recrystallized grain diameter more accurately. For the moment both the physical and semi-empirical relationships unified satisfactorily the grain diameters produced at higher or lower strain rates, however empirical approaches might give other alternatives.

7.4 Empirical Relationships and Recommendations

Empirical solutions have no physical justification and for that matter should not be used beyond the experimental range of conception. However in an effort to provide a solution to an important problem an empirical approach will be reported. Other researchers have recommended optimal hot working conditions that are also worth mentioning. In the future a more formal deduction may be discovered. One empirical method to predict the dynamically recrystallized grain size was derived using eq. 7.2. As with most Arrhenius relationships an activation energy can be determined that optimizes the correlation. An interesting fact is that the activation energy that best fits the D_{rex} - Z data is the same for the three coppers and the value is 413500J/mole. The fitted D_{rex} - Z data using this apparent activation energy for the nucleated volume is shown on fig. 7.5 and table 7.3 shows the values adopted by the constant K_{rex} and exponent n_{rex} . Table 7.3 also shows an improvement on the correlation coefficient, R^2 , see table 7.2 for comparison. The data used on eq. 7.2 originates from samples compressed only up to 0.8 strain hence supposing smaller grain sizes than the ones shown could be a mistake, because a complete dynamically recrystallized structure may not be possible below 0.8 strain. Only samples that had completely recrystallized were used (micrographs were taken on the middle line of compression about 4mm from the edge not in contact with the compression plates). When using eq. 7.2 either with the activation energy for self-diffusion or the apparent activation energy the amount of strain should be bared in mind, because the extrapolation that higher Z values produce smaller grain sizes may not be possible on the entire sample.

The recommendations made by several researchers for the optimal hot working conditions are difficult to generalize because recommendations tend to depend on the particular conditions used to study a type of copper. Camurri et al. [21] while studying a high oxygen (463ppm) fire-refined copper (no residual phosphorus reported) recommended hot rolling temperatures between 800°C and 900°C, strains >30% at strain rates <5s⁻¹. Ssemakula and Ståhlberg [22] reported the value of the finest grain size attainable (32µm) during extrusion at 750°C of a 99.98% Cu with 5 ppm of O after reaching 2.6 of strain. Ravichandran and Prasad [24] have recommended optimum parameters for hot workability based on the amount of oxygen and using efficiency power dissipation theories (some researchers readily accept power dissipation theories

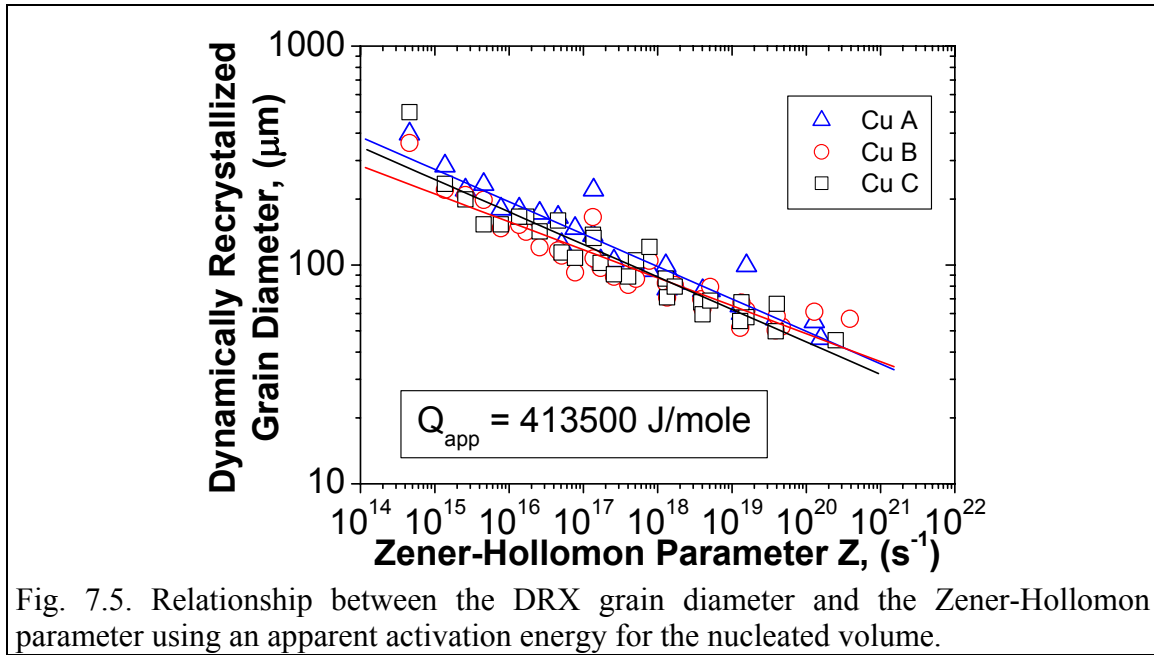


Fig. 7.5. Relationship between the DRX grain diameter and the Zener-Hollomon parameter using an apparent activation energy for the nucleated volume.

Table 7.3. Values of constants in eq. 7.2 but using an apparent activation energy.

	Copper A	Copper B	Copper C
Q_{app} , (J/mole)	413500	413500	413500
K_{rex}	45495.7	17488.4	41435.3
n_{rex}	0.148	0.128	0.148
R^2 using Q_{app}	0.902	0.873	0.889

others do not). Ravichandran and Prasad have said that in an attempt to avoid vacancy creation at hard particle boundaries and wedge cracking at triple junctions, coppers (with varying oxygen levels) should be worked at the so-called peak efficiency domains. The domains for OFHC coppers appear at temperatures from 900°C to 820°C and strain rates from 200s⁻¹ to 8s⁻¹, when the oxygen level is kept from 11ppm to 40ppm. However the domains for ETP coppers appear at higher temperatures from 825°C to 950°C but at lower strain rates (from 0.5s⁻¹ to 0.01s⁻¹) when the oxygen levels are from 180ppm to 260ppm. It is clear, from the work on this study that the final microstructure will depend on the type and amount residual elements, the amount of strain, the strain rate imposed and the temperature of deformation. Industrial processes do not have constant hot working conditions, however instantaneously the D_{rex} size will tend to the predicted size and reaching a homogeneous D_{rex} size on the entire volume will depend on the accumulated strain and the starting grain size.

The case of improving the room temperature mechanical properties of 99.9% pure copper has been presented, however ductility of copper also increases with a decrease of the residual content when coppers of higher purity are used [18]. Concerning 99.9% pure coppers some speculations exist about how certain cooling rates during casting allow the inclusions, partly composed of Pb, to absorb much of the impurity content leaving a purer surrounding area, which enhances formability.

7.5 Conclusions

- 1) The presence of Cu_2O precipitates enhances the nucleation of new dynamically recrystallized grains, however the presence of other residual elements may marginally be increasing the effect, particularly at higher temperatures. The two coppers with higher residual oxygen produced the finest dynamically recrystallized grain sizes.
- 2) The difference in dynamically recrystallized grain size is greater at temperatures above 850°C . At these temperatures the finest grain diameters were predominantly obtained with the copper with higher levels of Pb, Ni and Ag. However P, the most abundant residual element, also promoted a slightly finer microstructure at higher temperatures.
- 3) At temperatures below 850°C the final grain sizes of the coppers studied are almost the same, regardless of oxygen level or purity.
- 4) Prediction of the dynamically recrystallized grain diameter was possible using three different relationships.

7.6 References

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