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## Primary Recrystallization and Grain Growth of Tough Pitch Copper Wire

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**Résumé:** La classification des fils de cuivre "Tough Pitch" selon le taux d'impuretés est en général faite par l'essai d'allongement spirale. La sensibilité de la recristallisation aux impuretés est à la base de cet essai. Dans cette étude, des techniques pour caractériser la cinétique de la recristallisation, alternatives à la métallographie, sont considérées, comme la calorimétrie différentielle à balayage (D.S.C.; differential scanning calorimetry) et la résistivité électrique résiduelle. L'évolution de la recristallisation avec le taux d'impuretés est discutée. Dans une deuxième partie, la croissance discontinue des grains dans la barre laminée à chaud est mentionnée. Comme l'énergie libérée pendant ce processus est beaucoup plus petite que l'énergie associée à la recristallisation primaire, la D.S.C. est moins appropriée, une technique basée sur l'atténuation d'une onde ultrasonore est alors proposée.

**Abstract:** Tough pitch copper wire (99.97% Cu) is generally characterized by the spiral elongation number. The principle of the test is based on the influence of impurities on the recrystallization kinetics. Alternative non-metallographic techniques to characterize the recrystallization kinetics have been investigated in this study, such as differential scanning calorimetry (D.S.C.) and residual electrical resistivity measurement. The influence of different impurity levels on recrystallization is discussed. Furthermore, discontinuous grain growth in hot rolled rod is reported. As the heat released in this process is much smaller than in the case of primary recrystallization, D.S.C. is less appropriate to detect it and therefore a technique based on the attenuation of ultrasonic waves is proposed.

### 1. INTRODUCTION

The influence of impurities such as Se, Te and many others on the recrystallization behavior of copper has been recognized since many years. Earlier studies generally treat impurity contents of at least a few ppm [1][2][3]. Modern tough pitch copper production practice however allows to eliminate the most deleterious elements to less than ppm level. The question then arises whether the impurities still have an influence on the recrystallization behavior and so on the intrinsic wire drawability.

The results in this paper are compared to the widely accepted spiral elongation test, which reflects the degree of recrystallization after a standard heat treatment. It is observed that, for copper wires with very high purity, the wire is almost completely recrystallized after the standard heat treatment and the

discriminating character of the spiral elongation test is decreased. Some alternative techniques to discriminate the recrystallization behavior of good quality tough pitch copper wire are presented. In particular D.S.C. measurements (Differential Scanning Calorimetry) and residual electrical resistivity are discussed.

In a second part, a phenomenon of discontinuous grain growth is reported. The discontinuous grain growth occurs in tough pitch copper rod after a heat treatment in the temperature zone of 450°C to 600°C. The kinetics of this process seem to be related to the degree of impurity. It is suggested that the attenuation of an ultrasonic vibration is related to the volume fraction of the grains that have grown.

## 2. EXPERIMENTAL

The copper under consideration is supplied as continuously rolled copper rod of diameter 8 mm. The composition of 2 coils which were more closely examined, is given in table 1, while for the other coils the oxygen content ranged from 165 to 240 ppm and the total of all other impurities ranged from 7 to 38 ppm.

TABLE 1. Composition of the investigated copper as determined by arc spectrometry (in ppm).

	Pb	As	Sb	Sn	Bi	Fe	Ni	Co	Zn	Ag	Cr	Cd	Mn	Se	Te	S	O
Variety A (Sp-850 = 320)	0.9	1.2	1.2	0.5	0.1	1.8	5.3	1	1	11.4	0.5	0.1	0.1	0.3	<0.1	2.9	193
Variety B (Sp-850 = 25)	2.7	1.15	1.8	0.5	0.2	1.0	1.8	1	1	18.4	0.5	0.1	0.1	3.9	0.9	2.7	166

The thermomechanical preparation for the spiral elongation test, which is a standard test for the recrystallization behavior of copper wire, was as follows:

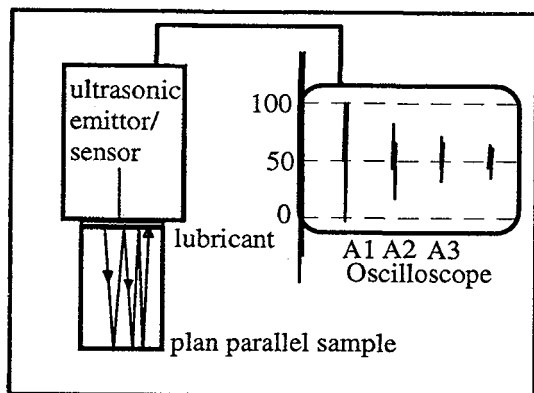


Figure 1: Set-up for ultrasonic attenuation measurement

- heat treatment of 30 minutes at 850°C + water quench
- pickle in HNO<sub>3</sub>
- wire drawing to 1 mm diameter in 18 steps
- recrystallization treatment of 2 hours at 200°C ± 1°C
- Sp-850 = spiral elongation (spiral diameter = 10mm, wire length = 1m, weight = 535 g)

The D.S.C. and electrical resistivity measurements were performed on drawn wire of 4.1mm resp. 0.51 mm diameter. A heat treatment of 30 minutes at 850°C, followed by a water quench, was carried out prior to the wire drawing, in order to eliminate the influence of hot rolling parameters. The recrystallization treatment mentioned for the Ø 0.51 mm wires was applied at 230°C for 5 hours.

A 910 D.S.C.-cell of T.A.Instruments was used for the D.S.C.-measurements at a heating rate of 10°C/minute. The bell jar was flushed with argon before the measurements to minimize oxidation. A recrystallized copper sample was used as reference sample.

An ultrasonic attenuation technique to evaluate discontinuous grain growth in a volumetric way is proposed. A rod sample is cut and ground plan parallel to a height,  $L$ , of 20 mm. A pulsed ultrasonic sensor at 5 MHz is pressed on the lubricated sample with a constant force of 9.8N. As the amplitude of the initial pulse cannot be determined directly, the amplitude of the first echo is set to 100 (arbitrary units

(a.u.)). The amplitude of the subsequent echos are measured and fitted to an exponentially decreasing function:  $A_n = A_0 \exp(-2nL/L_0)$ , where  $A_0$  and  $L_0$  are constants and  $n$  is the order of the echo. As the logarithmic decrement is  $\exp(-2L/L_0)$ , the damping is fully characterized by  $L_0$ .

### 3. D.S.C. MEASUREMENTS

D.S.C. measurements on wire drawn to 75% reduction (final diameter = 4.1 mm) were performed with the objective to evaluate the recrystallization kinetics. Two other phenomena appear at higher temperatures on the heat flux curve (figure 2).

A first exothermal peak is observed in the in the temperature interval between 200 and 300°C, when the energy stored during cold deformation is released during recrystallization. The position of the peak is very reproducible and permits several parameters of the recrystallization process to be studied.

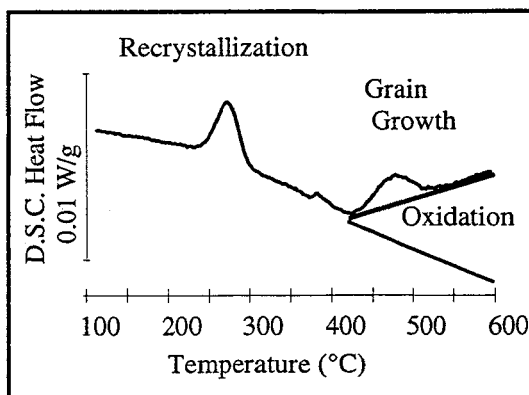


Figure 2: D.S.C.-curve of a copper wire drawn to 75% reduction ( $10^\circ\text{C}/\text{min}$ ), showing recrystallization, oxidation and a second peak from a process which occurs simultaneously with grain growth, such as redistribution of impurities or solution of precipitates.

At higher temperatures an exothermal inclination of the heat flow curve is observed, which is caused by oxidation, although care was taken to avoid oxygen in the cell. This effect blurs the other phenomena at higher temperature. The effect of oxidation is considered as being eliminated by measuring the same sample twice and subtracting the first curve from the second. The sample was ground in between the two experiments, so that the initial condition for oxidation was the same for both runs. A second peak remains nevertheless present on such a curve. Metallographical examination of the D.S.C. samples before and after the second peak confirms that this peak coincides with grain growth. As the heat flow of grain growth is much smaller than the heat flow of

recrystallization, other concurring processes must be considered, such as redistribution of impurities or solution of precipitates [4]. It remains unclear whether the growth process in wires is discontinuous as was observed in hot rolled rod.

The influence of impurity elements on the recrystallization peak is summarized in figure 3. Three characteristics of the recrystallization peak are compared for a series of copper samples with a varying impurity content: peak temperature (defined as the temperature at which the peak reaches a maximum), peak height and peak area. The main discriminating feature is the peak temperature, which decreases monotonously from low Sp-850 values up to Sp-850 = 310, where the slope suddenly increases tenfold. This justifies the hypothesis that the Sp-850-test loses its discriminating power for high purity copper wire because the wire is almost completely recrystallized when it is spiralled. Furthermore, the peak area, or the energy released during recrystallization, is constant ( $\pm 0.65$  J/g) and thus not related to the degree of impurity. The peak height, on the other hand, decreases for less pure copper. Considering that the peak area is constant, it can be concluded that a more impure copper has a broader peak. This implies that the impurities, either in solid solution or as small precipitates, exert a dragging force to such a degree that recrystallization is slowed down, even as the process takes place at a higher temperature and thus with a higher grain boundary mobility.

#### 4. RESIDUAL ELECTRICAL RESISTIVITY

According to Matthiessen's rule the electrical resistivity can be divided in two components: a thermal component, which varies linearly with temperature and is only dependent on the matrix material, and a residual component, which is determined by lattice defects such as dislocations, vacancies, solute atoms and precipitates. At room temperature the thermal component masks the residual component almost completely. Therefore the influence of the state of recrystallization and of the degree of impurity on the low temperature resistivity was evaluated (figure 4). The resistivity ratio  $r_{273K}/r_{10K}$  shows that the contribution to the residual resistivity of the cold deformation is more important than the contribution of the impurities. The results of the recrystallized samples are comparable with the residual resistivity ratio of an oxygen bearing copper with 9 ppm Se as unique impurity, as determined on a homogenized rod [3]. Variety A has a larger ratio than variety B, although the difference in resistivity ratio is small compared to the large difference in D.S.C. peak temperature between the two varieties.

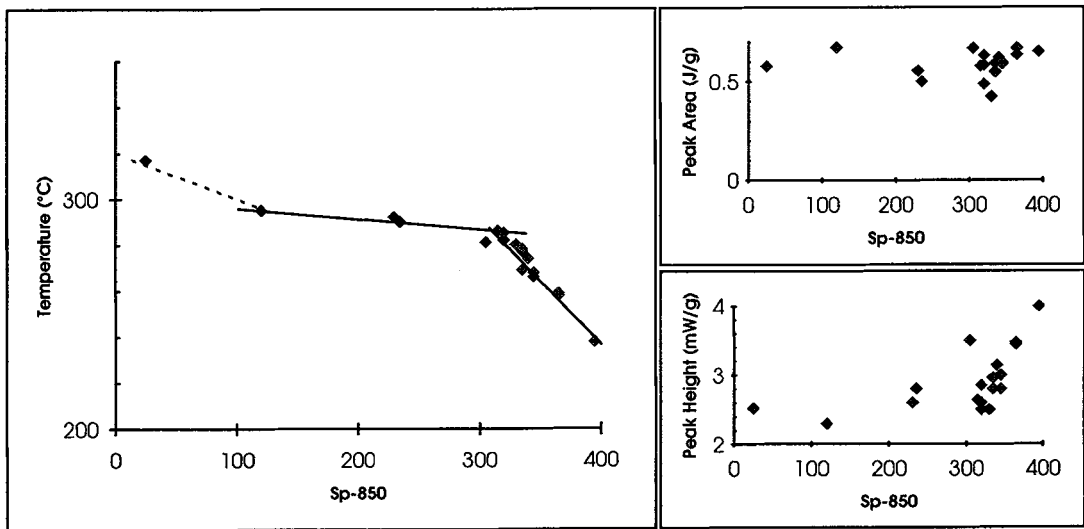


Figure 3: The influence of impurities on recrystallization is illustrated by the D.S.C. peak characteristics. The peak temperature decreases faster for high Sp-850-values and the peak height increases with a constant peak area.

TABLE 2: Resistivity ratios of the samples from figure 4 (cfr. Bigelow and Chen [3], where:  $r_{273K}/r_{4.2K} \cong r_{273K}/r_{10K}$ )

	$r_{273K}/r_{77K}$	$r_{273K}/r_{10K}$
a) Variety A	6.99	33
b) Variety A, recrystallized	8.45	184
c) Variety B	6.56	32
d) Variety B, recrystallized	8.36	157
311 ppm O, 9 ppm Se[3]	-	25
350 ppm O, 130 ppm Se[3]	-	206

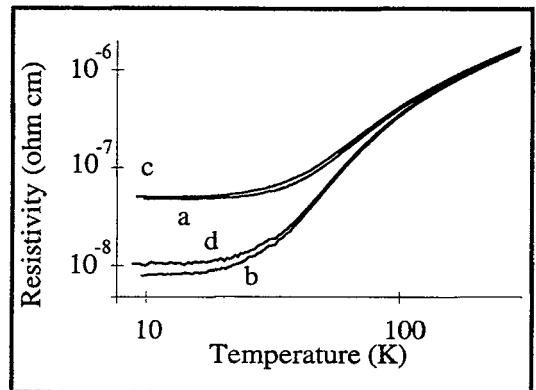


Figure 4: The electrical resistivity as a function of temperature: a) copper A, as drawn; b) copper A, recrystallized; c) copper B, as drawn; d) copper B, recrystallized

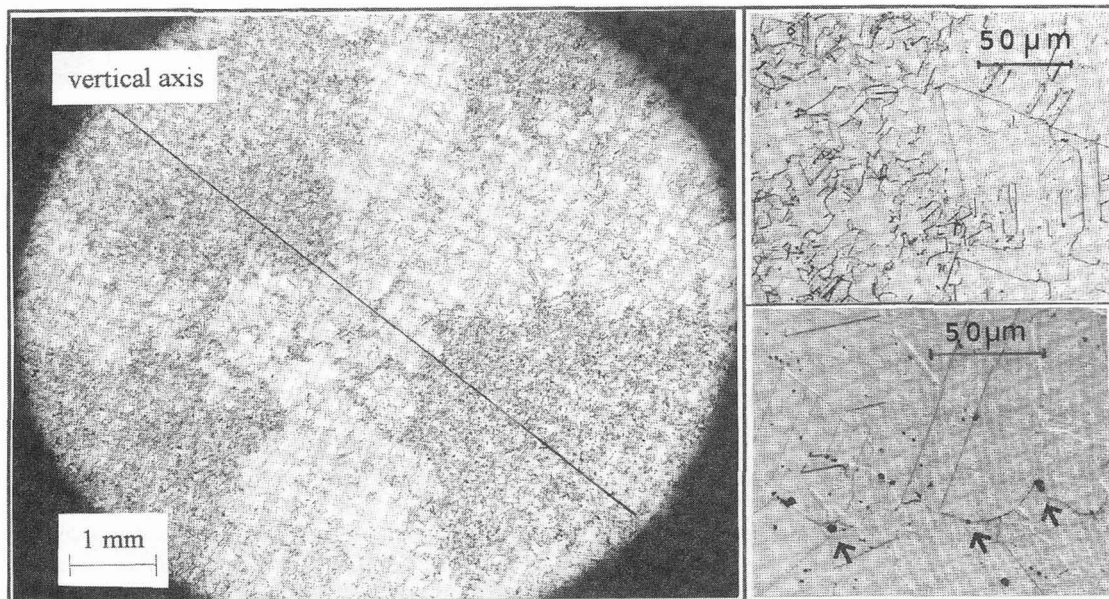


Figure 5: a. discontinuous grain growth in a transversal cross section of a hot rolled copper rod after a heat treatment of 5 hours at 500°C. b. magnification of a grain growth front in (a). c. same sample: the grain boundaries are pinned by cuprous oxide precipitates (black spots)

## 5. EVALUATION OF DISCONTINUOUS GRAIN GROWTH BY ULTRASONIC ATTENUATION

A case of discontinuous grain growth was observed while studying the recrystallization process (figure 5.a and 5.b). It occurs in hot rolled rod after a heat treatment in the range of 450 to 600°C. The regions in the rod cross-section to grow first are situated along the diagonals at 45° with respect to the rolls, i.e. the regions of redundant shear strain. Apparently some residual stresses are present after hot rolling, so that some preferential grain boundaries can migrate because they are locally less impeded by the cuprous oxides (figure 5.c). The less deformed areas, i.e. those (triangular) areas that touched the rolls, retain a stable grain size even after heat treatments that last many times longer.

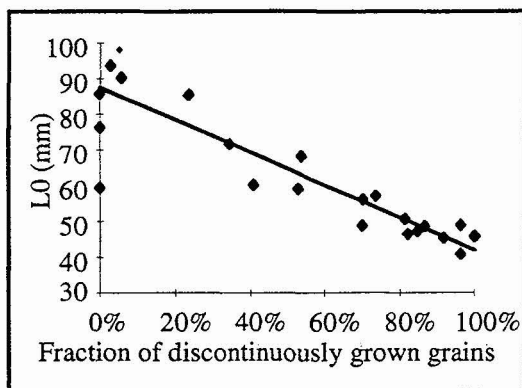


Figure 6: Correlation between the fraction of large grains as determined by optical metallography and the characteristic damping length,  $L_0$ .

The relation between microstructural properties and the ultrasonic response of metals has gained some interest in recent years[5][6]. The main advantage of the technique is that the result is averaged over a large volume. Usually the ultrasonic velocity rather than attenuation is discussed. The grain size distribution of a copper rod is however more marked by the variation of the damping of the wave than by the difference in ultrasonic velocity. In figure 6, the characteristic damping length,  $L_0$ , is given for rod samples with compositions A or B, after a heat treatment at 450, 500 or 590°C, of a duration of 2 minutes

to 24 hours. The fraction of large grains was determined by light optical metallography and a correlation was established between  $L_0$  and the fraction of discontinuously grown grains. With the  $L_0$  results a difference in kinetics for this process could be noted between variety A and variety B. To interpret this difference a better insight in the relation between the attenuation mechanism and the role of the impurities should be developed.

## 6. CONCLUSION

- D.S.C. measurements allow to differentiate between ETP copper varieties with only minor differences in impurity content. Prior cold deformation however influences the position of the recrystallization peak as well.

- The residual electrical resistivity is for this category of copper more influenced by the degree of recrystallization than by impurities.

- Discontinuous grain growth is reported in hot rolled rod. A correlation between the fraction of discontinuously grown grains and the attenuation of an ultrasonic pulse was established.

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