

## 2 Experimental Procedure

### 2.1 Material Preparation

The phosphorus deoxidised fire-refined coppers were supplied from the surplus material after a hot extrusion cycle for making copper tubing. The 99.9% pure coppers were first solidified into cylindrical billets of ~225mm Ø and ~510mm height. Then the billet was heated to ~950°C and inserted into a container or bolster as seen on fig. 2.1. As part of the process of making seamless tubing the billet was pierced (fig. 2.1a), which created a copper rod that served as a plug. When the piercer reached the die hole the copper would only extrude through the circular space between the piercer and the die. A forward push by the stem piston pressed the billet and tube began to form as seen on fig. 2.1b. Once most of the billet had been extruded, withdrawing the piercer as seen on fig. 2.1c created another plug. And finally the piercer protruded once again to cut the tube as seen on fig. 2.1d. The surplus copper left inside the bolster has been dynamically recrystallized due to the temperature and strain rate conditions of the process. A dynamically recrystallized grain size assures a relatively weak textured material and a considerably smaller grain size if compared to an only solidified billet. A picture of the supplied surplus copper is seen on fig. 2.2. The coppers had several residual elements, unlike OFHC or ETP coppers. However the purity is commercially high and the deleterious elements had been neutralized using elements like phosphorus. Three 99.9% pure copper billets were supplied at different times during this study and their total residual composition is seen on tables 2.1, 2.2 and 2.3 for the coppers named Cu A, Cu B and Cu C.

Table 2.1. Chemical composition of the 99.94% pure fire-refined copper A.

[ppm]	P	Sn	Pb	Ni	Ag	S	Fe	Zn	O	Sb
Cu A	297	86.2	63.5	31.7	30.8	22.0	17.2	15.6	26	14.1

[ppm]	As	Te	Cd	Se	Si	Bi	Co	Mn	Cr	Mg	Al
Cu A	10.7	9.61	6.67	3.84	2.46	1.67	0.79	0.57	0.31	0.08	<0

Table 2.2. Chemical composition of the 99.92% pure fire-refined copper B.

[ppm]	P	Sn	Pb	Ni	Ag	S	Fe	Zn	O	Sb
Cu B	253	120	169	54.3	46.5	9.8	16.3	31.3	46	25.6

[ppm]	As	Te	Cd	Se	Si	Bi	Co	Mn	Cr	Mg	Al
Cu B	9.09	13.5	3.79	4.12	2.94	3.41	1.20	0.63	0.33	0.08	0.02

Table 2.3. Chemical composition of the 99.95% pure fire-refined copper C.

[ppm]	P	Sn	Pb	Ni	Ag	S	Fe	Zn	O	Sb
Cu C	153	63.3	133	40.0	37.7	10.1	15.5	13.4	62	10.7

[ppm]	As	Te	Cd	Se	Si	Bi	Co	Mn	Cr	Mg	Al
Cu C	6.94	<0	0.49	1.29	23.2	2.04	0.73	0.56	0.40	0.10	0.08

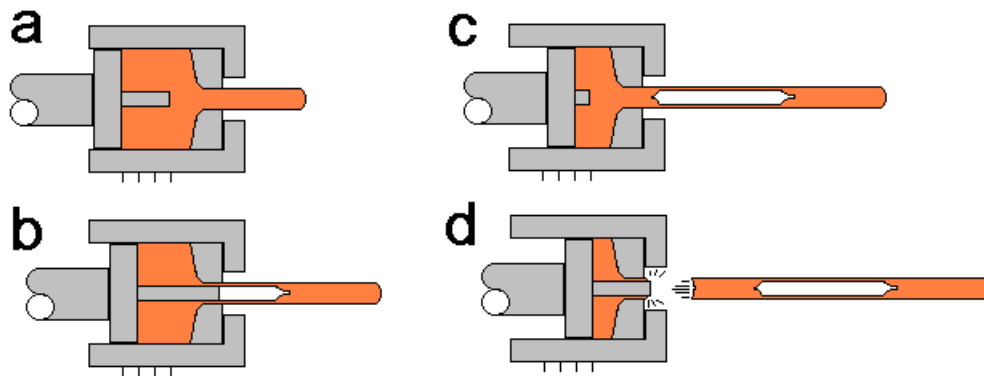


Fig. 2.1. Hot extrusion process for making seamless copper tubing. The material employed can be appreciated inside the container on fig. 2.1d. The process created a dynamically recrystallized copper surplus inside.



Fig. 2.2. A picture of Cu C as supplied in the extrusion surplus form.

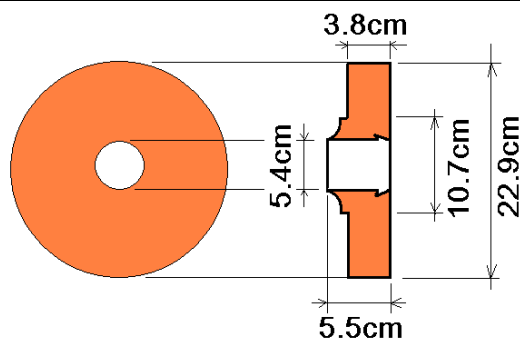


Fig. 2.3. Dimensions of Cu A in the supplied form.

An evaluation of the supplied microstructure was performed to assure an equiaxed grain and a particle free zone. The dimensions of Cu A in the supplied form can be seen on fig. 2.3. A radial slice was cut and a macro-metallography was created from Cu A. The macro-metallography showed a relatively equiaxed grain size, at least on the radial section. The grain size was small enough to produce small cylindrical

samples where many grains could be tested. Also a folded zone was identified on the corner in contact with the die that was furthest from the hole. On Cu B a smaller radial section was prepared and showed larger grains on the side that had been in contact with the die. For the latter reasons when the material was cut only pieces from the side free of folds or abnormal grain sizes were chosen. The billet was sliced using an oil cooled band saw seen on fig. 2.4. The copper bars were then sent to a machining workshop to produce test cylinders of 10mm  $\varnothing$  and 15mm height as seen on fig. 2.5.



Fig. 2.4. Oil cooled band saw used to slice the copper surplus material.

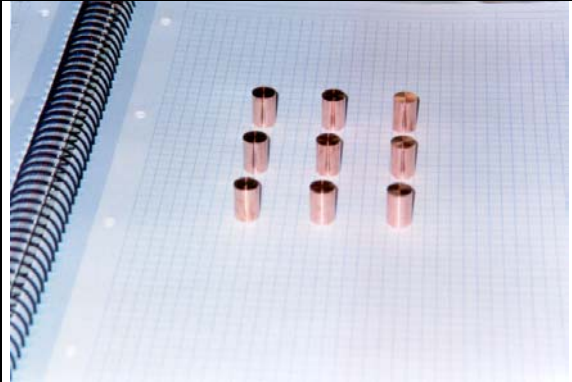


Fig. 2.5. As machined copper test cylinders measuring 10mm  $\varnothing$  and 15mm height.

### 2.2 Test Sample Annealing

Before performing hot compression tests the cylindrical copper samples were annealed as means of producing a relatively low dislocation initial structure that could be compared between the three coppers. Copper A was annealed inside the hot compression-testing machine before starting the test. The sample was introduced and when the thermocouple indicated that the temperature was 950°C the sample remained five minutes then the temperature was lowered to the testing temperature and the test began. In the case of testing at 950°C the test began after the five minutes. The assumption is that in the time the temperature lowered to the testing temperature the grain would not continue growing because drive force for growth at higher temperatures was not sufficient to keep growth at lower temperatures. In other words the dislocation structure difference on either side of a grain boundary is not sufficient to keep the grain growth that occurred at higher temperatures. Cu B and Cu C where annealed before introducing the samples into the hot compression-testing machine.

The other two coppers (Cu B and Cu C) were also annealed at 950°C with the aim of producing a grain size similar to the one obtained on Cu A. The tube furnace shown on fig. 2.6 was used to perform the annealing treatments of Cu B and Cu C. The grain size produced after annealing Cu B for 5 minutes at 950°C was of 570 $\mu\text{m}$ , which is slightly different from the 637 $\mu\text{m}$  of Cu A. In a parallel grain growth study [1], which will be shown on the results section, the grain size of Cu A after 5 minutes at 950°C was 409 $\mu\text{m}$ . However the value of  $D_0 = 637\mu\text{m}$  for Cu A will continue to be reported, because the value was measured from a test sample that was annealed inside the hot compression machine.



Fig. 2.6. Tube furnace and experimental setting used to perform the annealing treatments.

Table 2.4. Summary of the annealing treatments for Cu A, Cu B and Cu C before tests.

Copper	Time (min.) at 950°C	Grain size obtained, $D_0$ . ( $\mu\text{m}$ )
Cu A	5	637
Cu B	5	570
Cu C	15	530

Regarding Cu C the present author performed a grain growth study, which will be explained later, where 15 minutes were necessary to produce an initial grain size of 530 $\mu\text{m}$ . The annealing procedure for the three coppers before hot compression testing is summarized in table 2.4.

Annealing of the sample cylinders was performed in batches of four. The samples were dragged using a long metal wire to the center of the tube furnace at 950°C, and then a black rubber plug was used to prevent air from entering the tube (see fig. 2.6). The rubber plug had a copper tube in the center, which lead to a blue bucket of water where the bubbling indicated a pressured nitrogen flow. On the other end of the tube there was another rubber plug with a metal tube connected to a rubber hose, which supplied the nitrogen flow from a pressured tank. Once the temperature had reached 950°C the samples remained inside the furnace for five minutes and then were quenched in a bucket with water. The samples changed color only slightly and in some cases the grains could be appreciated. The annealed samples were now ready for hot compression testing.

### 2.3 Hot Compression Tests

The hot compression tests at constant strain rate were performed on an enhanced Instron 4507 electromechanical testing machine. Figure 2.7 shows a picture of the hot compression-testing machine. The schematic drawing on fig. 2.8 shows the original Instron machine. The constant temperature was achieved using a semi-electronically controlled furnace as indicated by shaded part on fig. 2.9. The furnace chamber was protected against high temperature corrosion using nitrogen gas as is indicated on fig. 2.10. The required true strain rate was achieved using software named “Administrador d’Assajos” [2]. The software operated from an external computer (see fig. 2.11), which also recorded the true stress-true strain data.

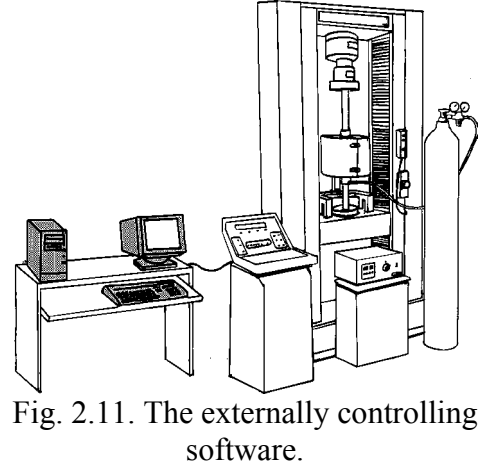
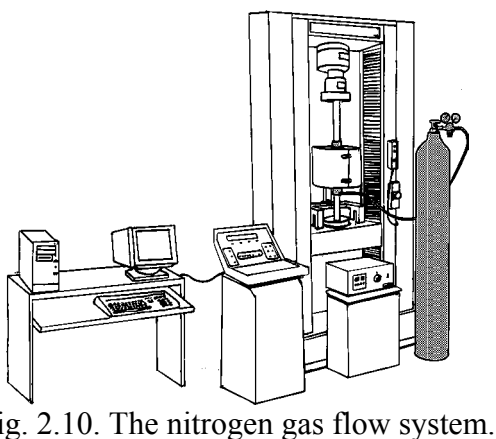
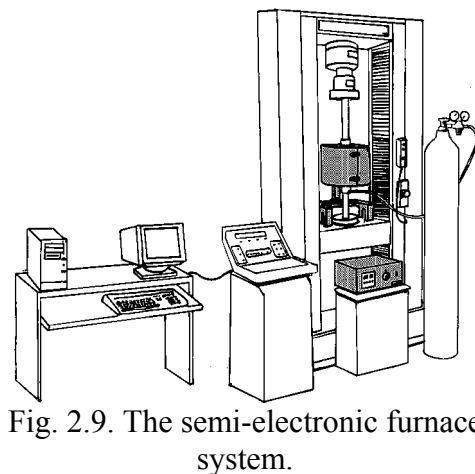
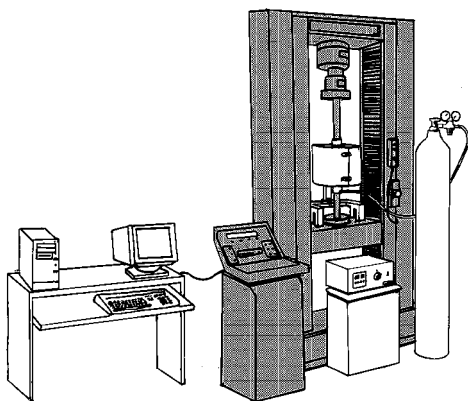
The hot compression tests were performed at eight different temperatures and six different strain rates for each of the three coppers. The temperatures ranged 600°C to 950°C in 50° intervals and the strain rates ranged 0.3s<sup>-1</sup> the fastest to 0.001s<sup>-1</sup> the slowest. Table 2.5 summarizes the temperature and strain rate conditions tested for each of the three coppers. Before the test the sample cylinders were covered with boron nitride, which served as lubricant, to minimize barrelling of the cylinder due to friction with the compression anvils (see fig. 2.12). The true strain achieved was 0.8. Figures 2.13 and 2.14 show a sequence of a compression tests at room temperature. Figure 2.15 shows the hot furnace exactly after a test when the compressed sample was quenched in a container with water (below the furnace). Quenching of the sample after the test lasted around 3 seconds. The compressed samples were saved for posterior microstructural analysis.

Table 2.5. Temperature and strain rate conditions tested for Cu A, Cu B and Cu C.

	600°C	650°C	700°C	750°C	800°C	850°C	900°C	950°C
0.3s <sup>-1</sup>	•	•	•	•	•	•	•	•
0.1s <sup>-1</sup>	•	•	•	•	•	•	•	•
0.03s <sup>-1</sup>	•	•	•	•	•	•	•	•
0.01s <sup>-1</sup>	•	•	•	•	•	•	•	•
0.003s <sup>-1</sup>	•	•	•	•	•	•	•	•
0.001s <sup>-1</sup>	•	•	•	•	•	•	•	•



Fig. 2.7. A picture of the equipment used for hot compression testing: an Instron 4507 electromechanical testing machine, an inert gas flow system, a semi-electronically controlled temperature and a software “Administrador d’Assajos” to maintain a constant strain rate.



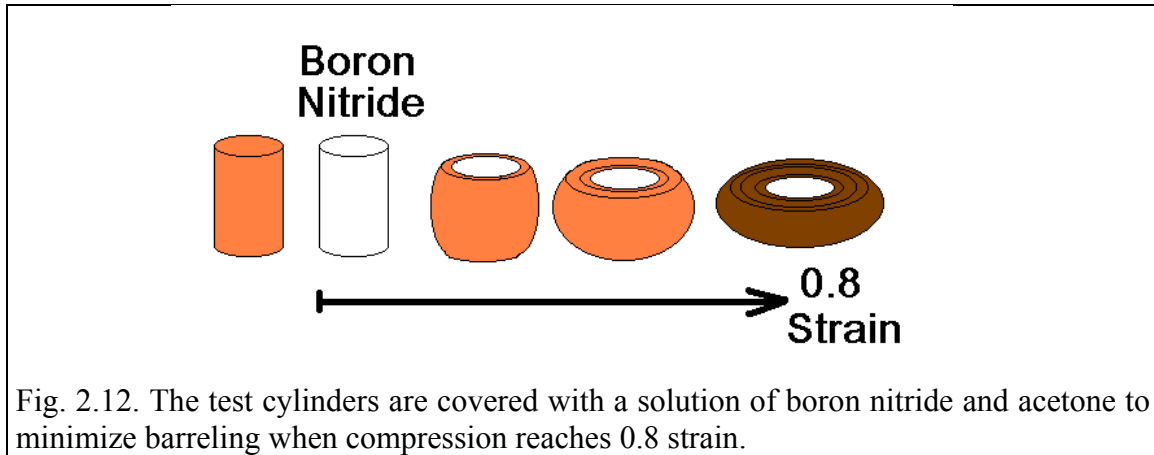


Fig. 2.12. The test cylinders are covered with a solution of boron nitride and acetone to minimize barreling when compression reaches 0.8 strain.

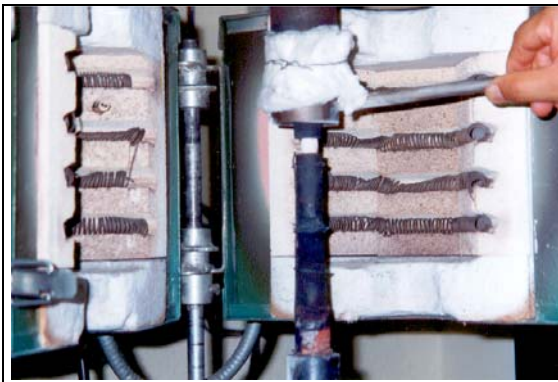


Fig. 2.13. The beginning of a compression test at room temperature allows visualizing the procedure.

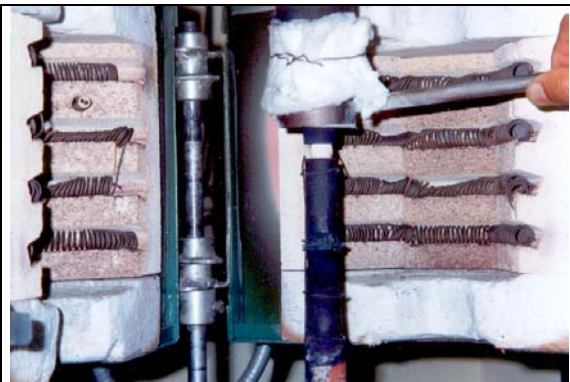


Fig. 2.14. The compression test that began in fig. 2.13 has continued straining the test cylinder.

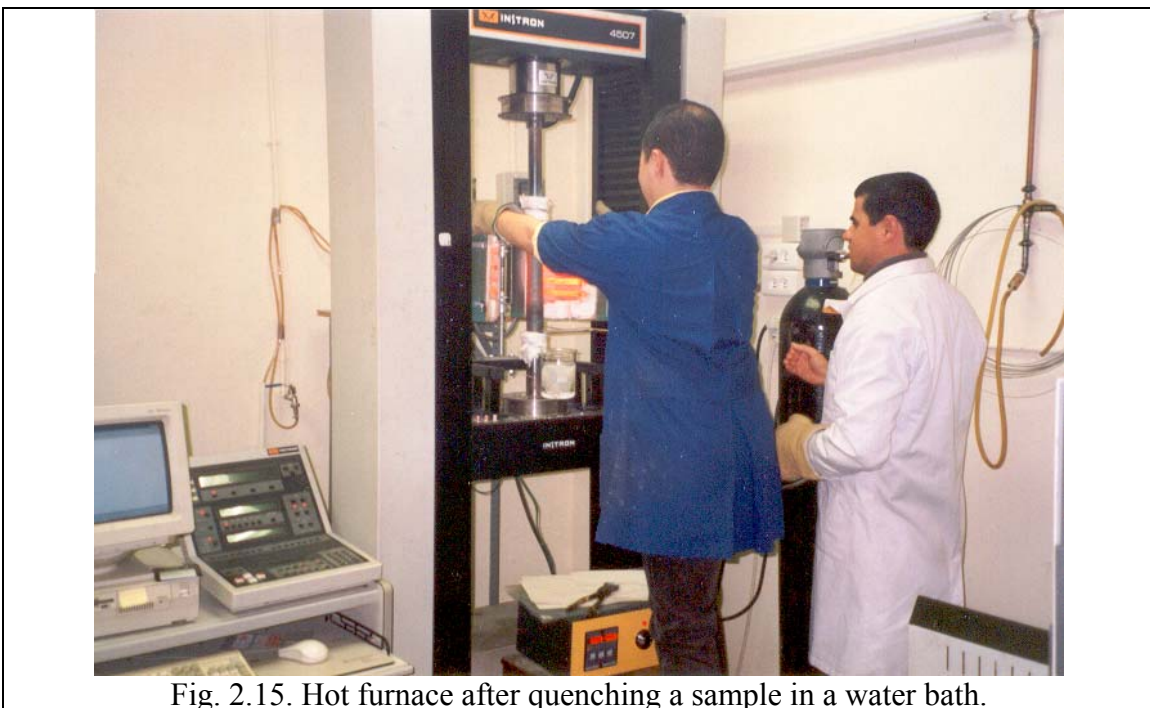


Fig. 2.15. Hot furnace after quenching a sample in a water bath.

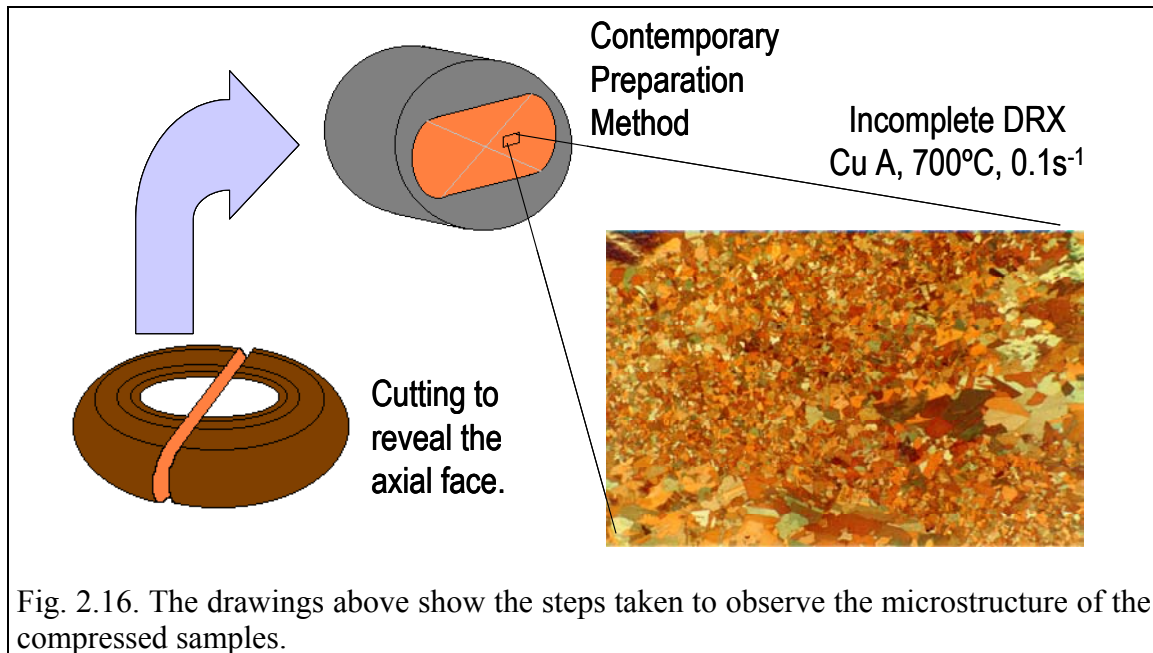


Fig. 2.16. The drawings above show the steps taken to observe the microstructure of the compressed samples.

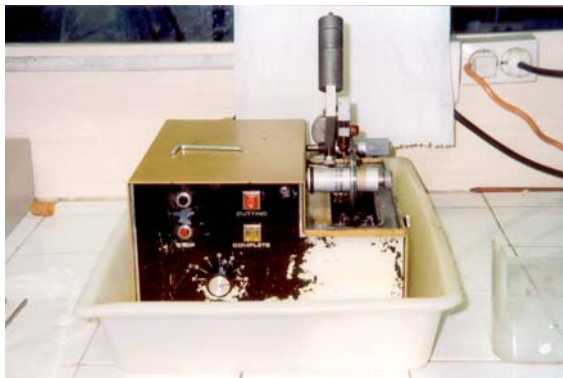


Fig. 2.17. Isomet precision diamond disc-cutting machine while slicing a compressed copper sample.



Fig. 2.18. Grinder-Polisher Ecomet 4 machine while polishing with diamond paste.

## 2.4 Metallographic Preparations

The final microstructure of the compressed samples was studied to obtain the dynamically recrystallized grain size for each set of conditions. First the samples were halved as seen on fig. 2.16 using an Isomet precision diamond disc-cutting machine shown on fig. 2.17. Then the axial face was thermo stable casted in Bakelite (at  $\sim 110^{\circ}\text{C}$ ) to be polished using a mechanical polishing method that is described in table 2.6. As seen on fig. 2.16 the samples were micrographed in the same place, in the middle line of



compression and about 4mm from the edge not in contact with the compressing anvils. An automatic “Variable Speed Grinder-Polisher Ecomet 4” machine was used during the sample preparation (cat. No. 60-1950-250). The grinding-polishing machine is seen on fig. 2.18. In all steps the black sample holder rotated clockwise and the polishing plate rotated counter clockwise. The commercial name of the polishing cloth was “Microcloth” made by “Buehler”. Steps (1) and (2) of table 2.6 used abundant water to wash out debris. The lubricant used on steps (3), (4) and (5) was named “Metadi Fluid” also from “Buehler”. A different cloth was used for each step that used diamond paste and only about two spoons of lubricant were used. In between diamond paste steps the samples were cleaned using non-abrasive liquid soap. Care was taken to soap the rim of the Bakelite using the tip of the fingers but without scratching the copper sample. For the first part of the cleaning process tap water was used for normal rinsing, but for the final rinse distilled water was used. On step (6) a pre-etching was performed in the manner to be explained. Step (7) where colloidal silica was used, care was taken not to drop crystallized silica on the cloth, because scratching would occur. Also during the 20 minutes required for silica polishing, attention was needed not to let the cloth become dry and small additions of colloidal silica were done. Step (8) is performed without stopping the machine, just by adding about 1.5 liters of distilled water at the cloth, not the sample holder (particles from previous use, stuck to the holder, might fall on the cloth). Once finished a hair dryer was used.

Table 2.6. Mechanical Polishing Technique to reveal the microstructure.

Abrasive Step	Plate speed (rev./min)	Force Applied (lb)	Time (min)
1) Grit P240	240	5	As required
2) Grit P1200	240	5	7
3) Diamond 9 $\mu$ m	140	5	15
4) Diamond 3 $\mu$ m	140	5	3
5) Diamond 1 $\mu$ m	140	5	1
6) Pre-etching			0.5
7) Colloidal Silica	140	5	20
8) Distilled water	140	5	10

The technique to chemically etch the samples during step (6) and for the final observation attempted to avoid a combination of over-etched and under-etched regions. The etching solution was prepared by mixing 70g of  $\text{Cl}_3\text{Fe} \cdot 6\text{H}_2\text{O}$  plus 210ml of HCl and 630ml of  $\text{H}_2\text{O}$ . For step (6) the samples were not to be withdrawn from the sample holder, because alignment would be lost. However the procedure is the same as seen on fig. 2.19, where the sample is placed upward with a meniscus of water on top so that when the three drops of etching solution are added the copper sample is not over-etched by the initial contact. A syringe filled with etching solution is used as a dropper. For step (6) at least 30 seconds of etching are needed. However for the last etch previous to the microscope observation only 7 or 10 seconds are needed. Afterwards a rinse using tap water, then with distilled water. Finally water drops were evaporated using a hair dryer.

If incomplete dynamic recrystallization was discovered then the micrograph was not used to measure the dynamically recrystallized grain size. Some of the micrographs were taken using polarized light, which colored the grains depending on the incident angle. The micrograph taken with polarized light seen on fig. 2.16 did not recrystallized completely. Only when a homogeneous grain size appearance was



Fig. 2.19. A meniscus of distilled water was placed over the polished sample and three drops of etching acid were added as seen on the picture.

micrographed, only then was the grain size measured using the line-intercept method or Heyn method. To measure the grain size a transparency that had two drawn lines, which crossed each other at  $90^\circ$ , was placed over each of the micrographs and the number of grains intercepted was counted. The grains not completely intercepted at the end of the lines counted as 0.5 each. The number of grains intercepted varied, for example, the minimum of grains intercepted was 11 and the maximum was 86. The sum of both lines was 200mm. The average grain size,  $D_{average}$ , was given by the following formula:

$$D_{average} = \frac{(Total\ length\ of\ the\ lines = 200000\ \mu m)}{(Magnification\ of\ the\ micrograph)(Total\ No.\ grains\ intercepted)}$$

### 2.5 Grain Growth Determination

Grain growth studies were performed on Cu A and Cu C, which would help determine not only the initial grain size before compression, but also would give an idea of the grain growth after a hot compression test instantly before quenching. The studies would also demonstrate if the residual composition played a decisive role during grain growth. For Cu C part of the supplied material seen on fig. 2.2 was cut into cubes of ~15mm per side. Care was taken not to over heat the cubes while cutting. The experimental setting to perform the grain growth study is the same as the one used for annealing the test samples seen on fig. 2.6. The temperatures and times selected for examination are shown on tables 2.7 and 2.8. Five copper cubes were introduced into the tube furnace at the selected temperatures and, past the required time cube by cube was withdrawn into a water bath. Some cubes fused together and more cubes were needed to complete the desired conditions on table 2.7. The flow of nitrogen gas protected the surface from high temperature corrosion. A picture of the differently colored surfaces after each set of conditions will be shown on the results section. Once the annealing treatments were performed the copper cubes were casted in Bakelite (at ~110°C) assuming that the casting temperature did not cause additional grain growth.

The procedure to polish the samples and measure the grain size has been explained in the section about metallographic preparation. A grain growth study [1] following the same procedure was also performed for Cu A.

Table 2.7. Temperatures and times for the grain growth studies of Cu C and CuA.

	5min.	10min.	15min.	30min.	45min.
600°C	•	•	•	•	•
650°C	•	•	•	•	•
700°C	•	•	•	•	•
750°C	•	•	•	•	•
800°C	•	•	•	•	•
850°C	•	•	•	•	•
900°C	•	•	•	•	•
950°C	•	•	•	•	•

Table 2.8. Additional Temperatures and annealing times for Cu C and Cu A.

	1min.	2min.	3min.	4min.
950°C	•	•	•	•
25°C	•	•	•	•

## 2.6 Inclusion Size and Distribution Determination

A study was undertaken to measure inclusion size and distribution, because inclusions may have been controlling or exerting an influence on the dynamically recrystallized grain size. Annealed uncompressed cylindrical samples of Cu A, Cu B and Cu C according to table 2.4 were polished using the steps of table 2.6 with the exception of etching, which would have dissolved the inclusions. Time after this study was performed, the author learned that 1µm diamond paste and then colloidal silica improved surface quality, but made inclusions jump out, leaving only a hole. The latter finding does not alter the results of this inclusion determination, because holes were counted and composition of each inclusion was not sought. However on the results section the composition will be reported. After polishing without etching the samples were observed with an optical metallographic microscope using 500X lens, and apart from dots difficult to be seen by the eye no inclusions could be determined. A Scanning Electron Microscope (SEM) was used instead to observe the polished surfaces, because the focus depth field is larger. A large enough depth field allows distinguishing more surface area at higher magnifications than the optical microscope. Each of the three samples was taped with a carbon containing film, which made the samples electrically conductive (a requirement in SEM that the Bakelite annuls). The samples were first observed from the surface of the cylinder and then towards the inside. Twenty continuous SEM micrographs were taken so that an area of 184616.5µm<sup>2</sup> could be examined on each copper sample. Approximately 19 micrographs were needed to fulfil the chosen area of 184616.5µm<sup>2</sup>. The SEM micrographs were taken at 1000X and 20kV. The micrographs were digitally saved and taken to a big screen monitor (~19inch) where with the use of a calliper the diameter of the globular inclusions was measured. The numbers were also counted. The viewed area was measured as well. Descriptive statistics was used to analyse the inclusion data for the three coppers.

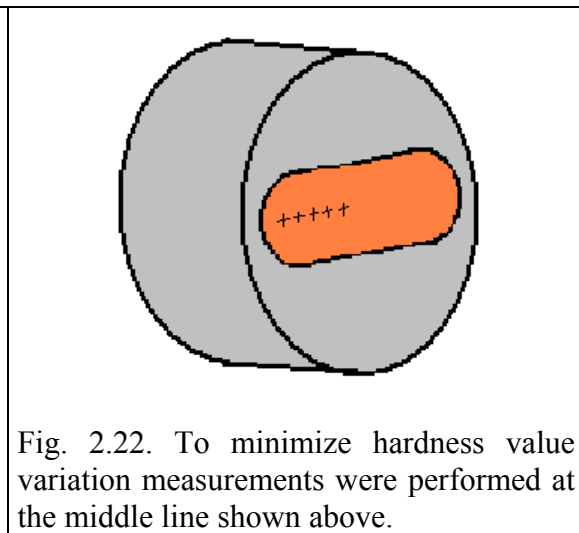
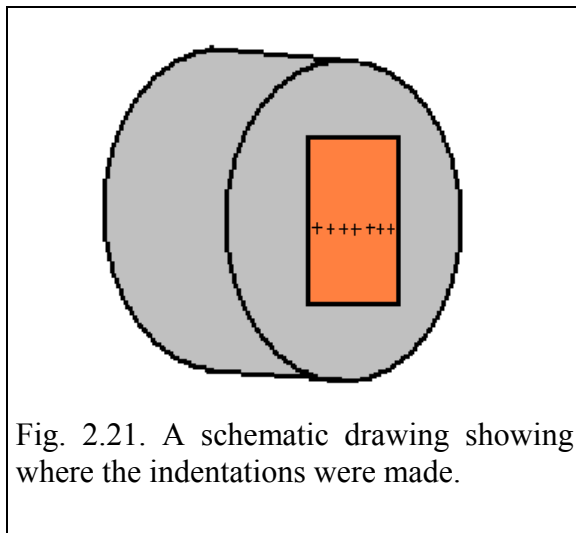
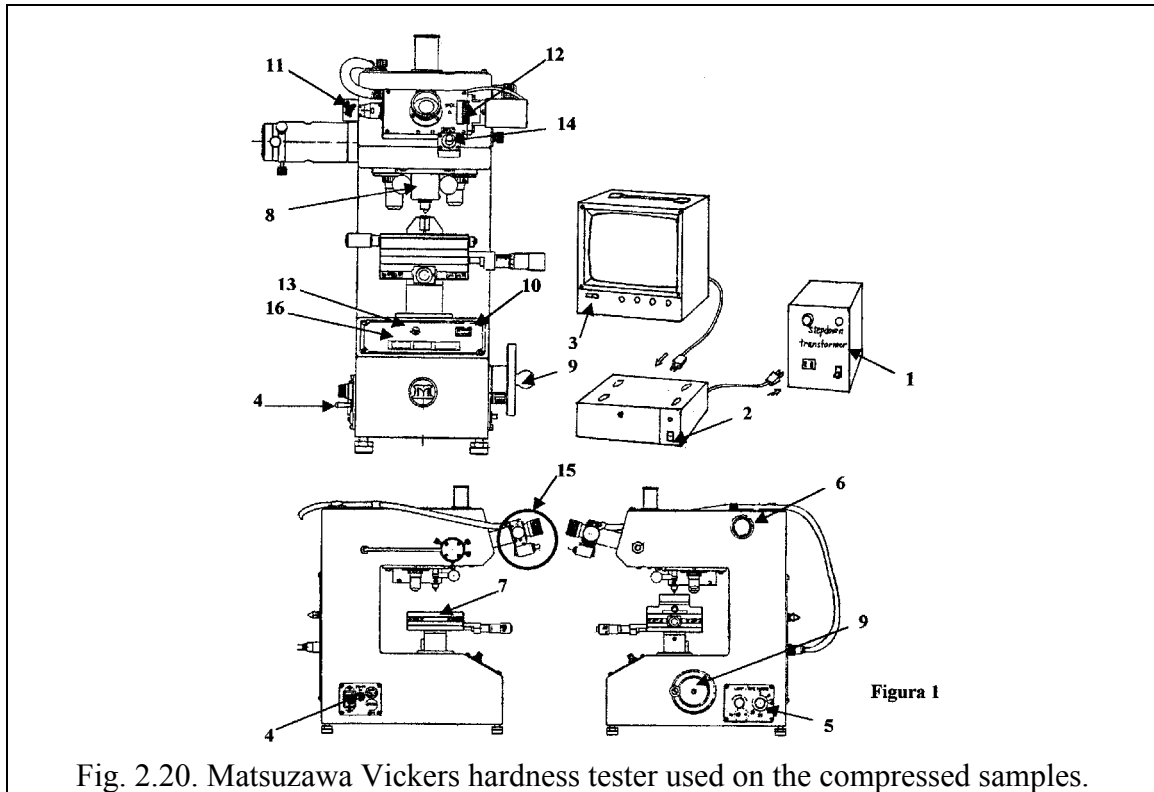
### 2.7 Precipitation Observations and Characterization

Results of the hot compression tests showed an increase of stress during hot flow when the oxygen content was increased, particularly at the lower temperatures tested. Never before had anyone inquired about the nature of the precipitates, if any, that caused a rise in the stress required for deformation. A microstructural investigation at a nanoscale was conducted using a Transmission Electron Microscope (TEM). Only six hot compressed samples were chosen for examination. A compressed sample was selected of each copper tested at,  $0.3\text{s}^{-1}$  and  $900^\circ\text{C}$ , which was a high enough temperature for stress differences to be minimal. Other three compressed samples were chosen at  $0.3\text{s}^{-1}$  and  $750^\circ\text{C}$ , a temperature where the stress differences were noticeable. Three different thinning techniques were employed to obtain the thin foils required for viewing fine precipitates through TEM. These three techniques were necessary to rule out the creation of fine particles during the preparation of the TEM samples. Ring patterns or Debye-Scherrer rings had been used in the past to determine the formation of  $\text{Cu}_2\text{O}$  in copper powder [3, 4]. Ring patterns have also been used to determine fine copper second phases [5]. This characterization procedure also attempted to use the known relationship between the diffraction ring diameter and the inter-atomic spacing, which has been calculated earlier by other researchers. Inter-atomic spacing is characteristic for each crystallographic material.

Fire-refined coppers possess a number of residual elements, which could react with some electropolishing electrolytes and form misleading fine crystals. Care had to be taken to avoid forming oxides during the TEM sample preparation. The first electrolyte tested, using a Struers Tenupol-3 jet electropolishing machine, was a solution of 54% orthophosphoric acid and 46% deionized water. The potential employed was 8V at  $20^\circ\text{C}$ . A second electrolyte used was a solution of 80% methanol and 20% Nitric Acid. The potential was 2.5V at  $-20^\circ\text{C}$ . The ion milling technique was used to finally rule out the formation of fine crystals by a chemical reaction with the other two electrolytes. A “Dimple Grinder Model 656” made by “Gatan” was used to micromill a cavity using  $9\mu\text{m}$  diamond paste. Then to make the final thinning a “Precision Ion Polishing System Model 691” made also by “Gatan” was used. However the latter technique produced a nanograined microstructure, which only offered information as to how many rings truly belonged to the fire-refined copper and the possible precipitates (ring patterns were produced during selected area diffraction in the presence of two types of nanocrystals).

### 2.8 Hardness Measurements of the Final Microstructure

After measuring the dynamically recrystallized grain size on the compressed samples, measuring the room temperature mechanical properties would have been desirable, however the size of the deformed sample did not allow other tests than hardness tests. Hardness is not a mechanical property, but efforts have been done to correlate the hardness to stress-strain related properties. Hardness is the property that describes the resistance of a material when being penetrated by another material. Vickers hardness tests were performed using a “Matsuzawa Seiki” tester “Model DMH-1” (as seen on fig. 2.20) equipped with television screen to measure the diagonals of the imprint. Initially hardness was measured on the same annealed and uncompressed samples used for inclusion study. A finding that modified the hardness measuring



procedure was that hardness following a line perpendicular to the axial direction as seen on fig. 2.21 produced softer values near the extremes than in the center. The author supposes there could be a depth effect that causes that the indentations near the center to have a higher value than the rest. Probably not enough material lies beneath the indentation to produce an accurate reading. Bearing in mind the latter observation, hardness was measured on a middle line of the compressed samples between the flat sides of the sample as indicated by fig. 2.22.

Vickers hardness measurements were performed on the polished samples described on table 2.5 for the three coppers. The indentation load was 500g. The indentation time was 30 seconds. On each compressed sample five measurements were taken, as explained, following a middle line. The described procedure minimized

variations on the hardness readings despite indenting either on one or many grains regardless of the compression temperature. The hardness value to be reported in the results section is the average of the five measurements performed on each sample.

The same hardness measuring procedure was performed later on solubilized (1000°C) and then aged samples for precipitation determination, but the results were non-conclusive.

### 2.9 References

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