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Secondary Recrystallization in Copper

James E. Thompson

SECONDARY RECRYSTALLIZATION IN COPPER

A Thesis

Presented to

the Faculty of the Department of Metallurgy

Montana School of Mines

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science in Metallurgical Engineering

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INTRODUCTION AND PURPOSE

"Secondary recrystallization" is a phenomenon by which large grains or crystals (these two terms will be used interchangeably throughout this thesis) are developed in a specimen that has been heat-treated above the recrystallization temperature for a period of time.

For the most part, these large grains are not desirable in commercial practice because of the undesirable properties of large grains. Secondary recrystallization studies are used to explain the phenomenon of secondary recrystallization and as an aid in studying primary recrystallization.

The purpose of this thesis is to study the conditions under which secondary recrystallization will take place in copper. The variables considered were the time of annealing, the temperature of annealing, and the degree of cold work undergone by the specimen before it was subjected to the heat treatment.

Many investigations have been carried out on copper, aluminum, and brass. Some of these investigators(2, 6, 8, 10, 11) have studied the orientations of the grains in specimens both before and after secondary recrystallization occurred. Others(3, 4) have studied secondary recrystallization from the standpoint of heat treating time, heat treating temperature, degree of cold work, and the different methods of achieving the desired cold work.

The reason that an orientation study was not made was that the previous investigators have generally agreed on the orientations found in copper.

PREVIOUS WORK

The driving force for secondary recrystallization has not been adequately explained by any theory advanced to date. At the present time, there are two basic theories; one is based on nucleation of the secondary grain in a highly deformed area of the specimen, and the other theory is derived using a combination of stacking fault energy, energy from grain boundary disappearance, and a change in surface energy, as the driving force for secondary recrystallization.

Almost all previous investigators found that over 90% reduction in thickness was necessary for secondary recrystallization to occur in any copper specimen. Since this reduction is necessary, a description of what happens to the material as it passes through different stages of reduction is necessary. This description is as follows: Up to about 50% reduction, the crystals align themselves in the preferred orientation that will be the resultant texture. The plastic deformation necessary for this 50% reduction is accomodated by the slipping of each individual crystal along its slip plans, and this slip process brings nearly all the grains into the preferred orientation. After 50% reduction, the grains begin to break up into blocks. As the degree of reduction becomes greater, the size of the resulting blocks becomes smaller.(6) These blocks result in a cubically-aligned twinned structure.(6) This twinned structure is believed to be necessary for secondary recrystallization because no secondary recrystallization was observed in twin-free cubically-aligned copper.(11)

After seeing how copper is deformed during cold working, it is easier to understand the theories that attempt to explain secondary recrystallization.

One of the theories on how secondary recrystallization comes about was proposed by Bowles and Boas(3), and their theory is based on the concept of nucleation of the secondary grains.

The basis of Bowles and Boas's theory is that upon heating of a specimen in the range necessary for secondary recrystallization, strain free nuclei are formed in the most severely deformed regions of the specimen by true nucleation. To explain how the secondary grains grow, Bowles and Boas say "that during primary recrystallization, a redistribution of internal stresses occurs, and that the growing primary crystals are therefore put into a state of internal stress or perhaps even plastically deformed. At the same time, stresses in the unrecrystallized material are relieved to some extent by this redistribution and also by recovery. Thus, although the growing primary grains are originally the most perfect and therefore the most stable parts of the specimen, they do not necessarily remain so. When they become less stable than the most perfect parts of the deformed metal, the latter will tend to grow at the expense of the primary grains, i.e., secondary recrystallization will occur."(3)

The reasons for formulating this theory are as follows: (1) it was found that both the orientation of the primary recrystallized texture and the orientation for the secondary recrystallized texture existed in the deformed specimen before annealing. (2) the orientation found in the most heavily deformed material was similar to the orientation of the secondary recrystallized grains, and it was not similar to the orientation of the primary grains. (3) this theory is independent of any theory used to explain primary recrystallization.(3-518)

Although this theory is plausible, there is an assumption made in the derivation that may or may not be true. This assumption is that nucleation of the secondary crystals does occur in the severely deformed metal.(3-517) It has not been proved conclusively whether nucleation does or does not occur in a metal under the conditions of the theory.

Another theoretical explanation of secondary recrystallization was advanced by Kronberg and Wilson after an extensive study of secondary recrystallization in copper. The basis of this theory is that a few structural changes in the metal lowers the free energy of the metal, and this lowering of free energy acts as the driving force for secondary recrystallization.

The first conclusion that Kronberg and Wilson arrived at was that secondary recrystallization did not occur in twin-free samples after annealing for six hours at a temperature of 1050° C. This heat treatment was sufficient to cause complete secondary recrystallization in all twin-bearing samples of similar reduction.(11) From this experiment, Kronberg and Wilson concluded that the energy associated with the stacking fault existing at a twin boundary is probably involved in the driving force and activation energy for secondary recrystallization.(11)

Another, and most probable, driving force for secondary recrystallization, according to this theory, is the disappearance of grain boundaries which lowers the free energy of the specimen, thus promoting secondary recrystallization.(11)

A third possible driving force arises from the fact that there is a change in orientation altering the geometric distribution of atoms at the surface of the specimen, and if this lowers the surface tension, the corresponding decrease in free energy would contribute to the driving force for secondary recrystallization.(11)

A still further possible contribution to the driving force came to light when the investigators found that secondary recrystallization initiated at the surface of the specimen. At the surface of the specimen, the atoms have the greatest amount of movement and are correspondingly more energetic. This fact was interpreted to mean that the energy associated with the surface atoms probably contributed to the driving force.(11)

Since no adequate explanation of the phenomenon of secondary recrystallization has been advanced to date, either of the two preceding theories or any other proposed theory could be partially or wholly correct. Only further research will prove which, if any, is the correct explanation for secondary recrystallization.

APPARATUS

Since no suitable furnace for heat treatment in a controlled atmosphere existed in the laboratory, it was necessary to construct such a furnace so that the specimens would not oxidize during the heat treatment. Also, since the specimens used were thin (about 0.02 in.), it was necessary to set up an electropolishing apparatus to obtain specimens with a scratch-free surface so that the specimens could be examined by microscopic techniques.

Figure 1 is a photograph of the controlled atmosphere furnace and its accessories. The furnace itself consists of a ceramic tube 14 in. long and 2 in. inside diameter. Around this tube are wound three separate and equal size coils of Kanthal wire. Insulation for the furnace is provided by 9 x 4.5 x 2.5 in. insulating bricks which completely surround the ceramic tube. Further insulation is provided by 3/8 in. asbestos sheet that completely surrounds the bricks. A Variac is used to control the current into the furnace thus permitting temperature control.

To insert the glass tube shown in Figure 1 into the furnace, holes were cut in the asbestos and the bricks at the same level as the center of the ceramic tube. This glass tube is 3 ft. long and has an inside diameter of 1 in. The inlet end of the tube has a thermocouple sealed in it and provides an inlet for the atmosphere used in the furnace. This atmosphere is discharged through the outlet end of the tube. Another use for the outlet end is charging the furnace.

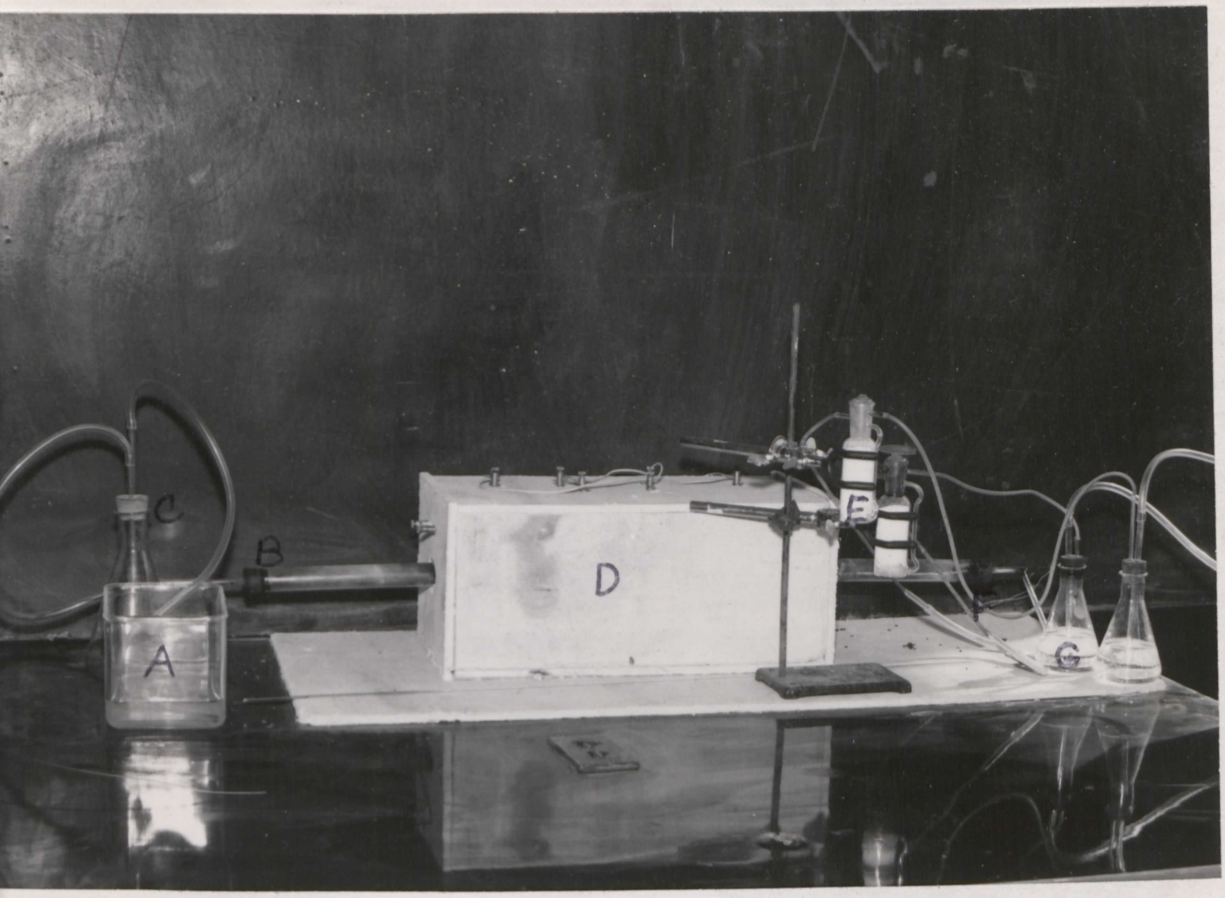

Figure 1. A Photograph of the Controlled Atmosphere Furnace and its Accessories.

A. Water Trough

B. Outlet End

C. Water Trap

D. Furnace

E. Calcium-Chloride Dryer

F. Inlet End

G. 250-ml Erlenmeyer Flasks

The atmosphere entering the furnace is a gas composed of approximately five parts nitrogen to one part hydrogen. This mixture of gases was used because of the reducing properties of hydrogen and because nitrogen dilutes the hydrogen making it less dangerous and reducing the amount of the more expensive hydrogen used per run. Each of the gases comes from its own tank, and then each gas passes through a 250 ml Erlenmeyer flask containing concentrated sulfuric acid which acts as a drying agent and as a control on the amount of gas entering the system. After passing through the sulfuric acid, each gas passes through a calcium chloride dryer, and finally the gases mix and enter the system.

After the gases pass through the system, they leave the system at the outlet end. Upon leaving the system, the gases pass through a water trap. From the trap, the gases go into a water trough and enter it below the water line. This trough is necessary because it gives an immediate indication of whether or not there is a positive pressure forcing the gases through the system.

Another use of the outlet end, besides removal of gases, is the charging of specimens. Specimens may be charged into the furnace when it is cold and the gas supply is shut off by removing the rubber stopper in the outlet end and pushing the specimen into the desired location inside the furnace with a glass rod. A provision was also made for charging the furnace when it is hot and the gas is passing through it. All that was done was to pass a stiff wire through the rubber stopper in the end of the glass tube. Thus, when the furnace reaches the desired temperature, the wire is pushed into the furnace the required distance and the specimen is in the desired position provided the specimen was attached to the wire before it was heated up.

Before the nitrogen-hydrogen atmosphere was put into use, a vacuum system was tried. The only changes in this system and the system shown in Figure 1 were that the vacuum pump was attached to the gas inlet and a Pirani gage was placed at the outlet to measure the vacuum. The best vacuum obtained in the system was 26 microns, but this vacuum was insufficient to prevent oxidation of the copper.

Because of the thinness of the specimens (about 0.02 in. thick) used in the tests, the normal metallographic techniques could not be used to prepare the specimens. Instead, a method of polishing called electropolishing was used to prepare the specimens. In electropolishing, the current removes the metal from the high points on the surface of the specimen (the anode) and deposits this metal at the cathode. The electrolyte used for electropolishing copper is made up of 453 gms of orthophosphoric acid per liter of water. The current and voltage across the cell for efficient operation are given on page 901 in the Metals Handbook. The circuit used to obtain the desired voltage and current is shown in Figure 2, page 11. Before any electropolishing is done, the specimen is taken down through 4/0 paper in the usual manner.

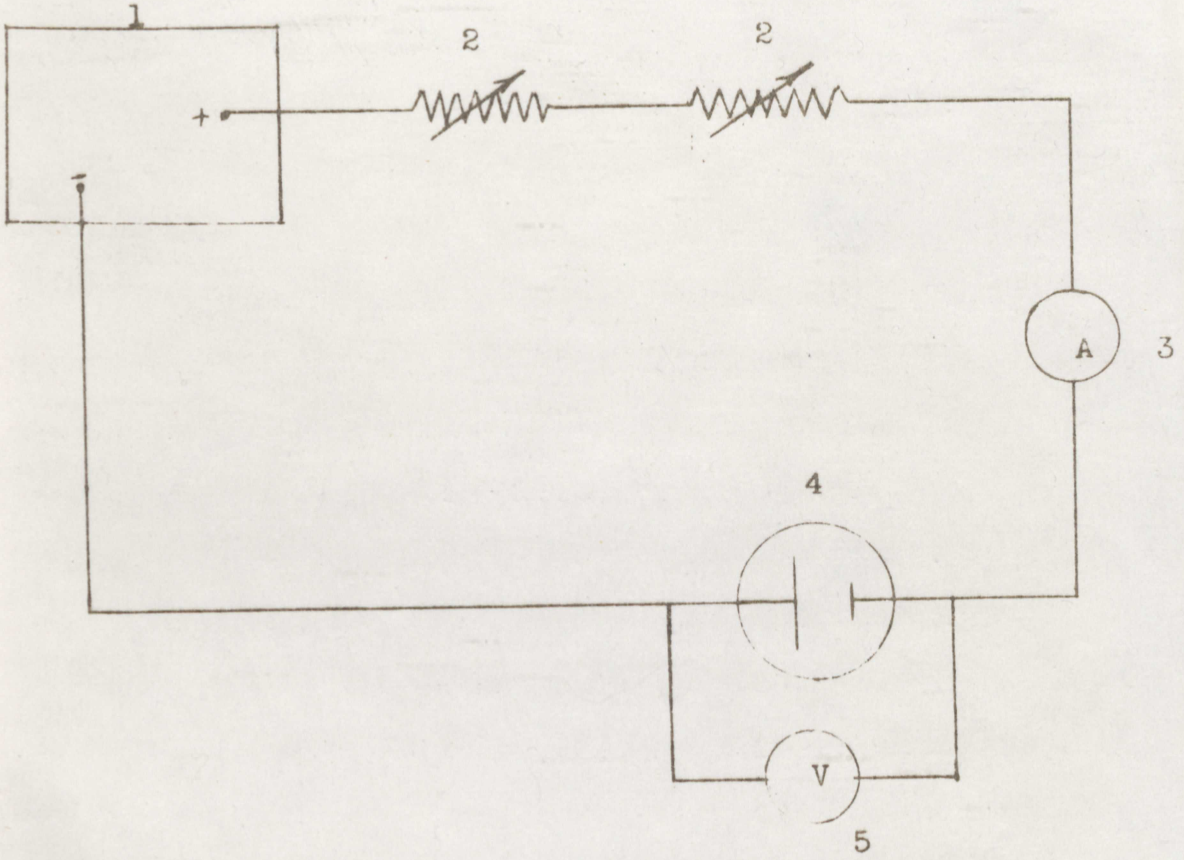

Figure 2. A Sketch of tne Electropolishing Circuit.

1. Six-Volt Battery
2. Variable Rheostats
3. Ammeter
4. Cell
5. Voltmeter

RESULTS

The results of the tests to achieve secondary recrystallized structure in copper are given in Table I on page 13. Each sample that was prepared was labeled alphabetically. Some of the earlier specimens were omitted from the table because they were oxidized in earlier tests using the vacuum system in the furnace. Other specimens were omitted from the table because they were used as checks or were used to test different polishing and etching techniques. All specimens designated as being prepared from the original sheet came from a thin copper sheet that was at first believed to have been cold-worked a sufficient amount to promote secondary recrystallization. The actual degree of cold work of the sheet was not known. All other specimens came from a commercially-pure copper rod 1/2 in. in diameter. All specimens were 1 x 0.75 in. with the long side parallel to the rolling direction. Since the rolling direction in the original sheet was not definitely known, a direction was assumed to be the rolling direction from the scratches on the sheet, and this direction was used consistently.

Another reason for using the original sheet, besides the assumption that it was cold-worked sufficiently, was that there was not a sufficient set of rolls in the laboratory to give reduction of over 90% and still have a specimen that could be handled easily. To obtain the high reduction for the last specimens, a sample from the copper rod about 0.7 in. long was compressed in a Tinius-Olsen 100,000-pound machine to a thickness of approximately 0.2 in. (a 71.5% reduction), and then passed through a set of rolls, using the straight-roll method, until the desired reduction was achieved.

RESULT OF TESTS USED TO ACHIEVE SECONDARY RECRYSTALLIZATION

		Heat Treatment		
Sample	Preparation	Time Hrs.	Temp. °F.	Comments
I	Original Sheet	5	1370	Annealed grain structure.
J	" "	10	1355	" " "
L	" "	20	1340	" " " No appreciable grain growth in 20 hours over 10 hours.
O	" "	30	1030	Annealed grain structure.
R	35% reduction Straight rolling	44	1200	" " "
S	Original Sheet	44	1200	" " "
R	Same as before	41	1200	No grain growth in last 40 hours.
S	" " "	41	1200	" " " " " " "
V	88.5% reduction	26	1085	Annealed grain structure.
T	97.5% reduction	39½	1120	Annealed, fine grain structure.
X	97% reduction	48	1890	Annealed, fine grained structure.
Z	98.2% reduction	48	1890	Secondary recrystallized structure.
AA	" "	48	1890	" " "
AB	Original Sheet	48	1890	Annealed grain structure.

Since the annealed structure is mentioned throughout Table I, a photomicrograph of an annealed structure, sample L, is given in Figure 3. The etchant used was a Dichromate etch followed by a Ferric Chloride etch. This etch was used on all samples unless otherwise indicated. The large width of the grain boundaries is believed to be due to thermal etching after primary recrystallization had ceased.

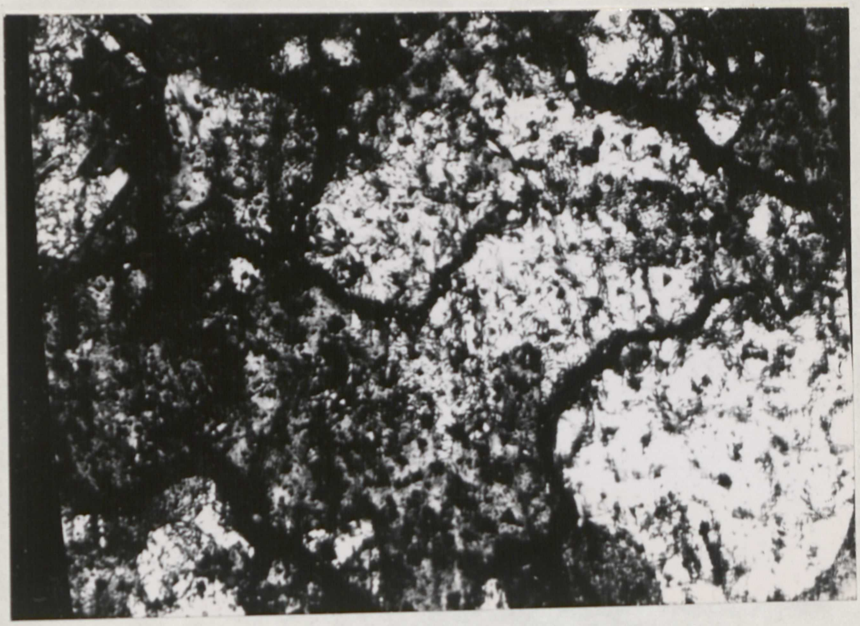

Figure 3. An Annealed Structure in Copper (Sample L)
Magnification 150x

All results indicate that the specimens from the original sheet would not undergo secondary recrystallization under any conditions of the tests. Therefore, probably none of these specimens would exhibit any secondary recrystallization if heated for a greater length of time at about 1890° F. because other investigators (3, 8, 11) found that secondary recrystallization was complete in about one hour at temperatures above 1800° F. if the reduction were sufficient enough to give secondary recrystallization. Therefore, the sheet did not undergo a great enough reduction without annealing or no twins were formed or a combination of both. The first explanation is the most probable one because the sheet was not as difficult to bend as the highly-worked specimens. Since ductile metals become harder and brittle when severely cold-worked, this bending test can be used as an indication of the degree of cold work that a ductile metal, such as copper, has undergone. Also, twins were observed in microstructures in some specimens, from the original sheet after the specimens had been heat treated.

As can be seen in a comparison of samples Y and Z in Table I, secondary recrystallization occurred at the same temperature for a slight increase in the per cent reduction. Two possible explanations for this difference are the greater reduction in Z and the lack of twins in Y. It should be noted that both samples came from the same piece of copper rod with sample Y being cut off when 97% reduction was achieved, and the remaining sample being reduced to the thickness of sample Z. After the heat treatment, there was no twinned structure visible in Y, while one was observed in Z. However, this does not mean that twins were not present in Y because the grain structure was so fine that it would have been difficult to observe any twins if they were present. It must be assumed that secondary recrystallization occurred in Z but not in Y because of the difference in the per cent reduction for the two samples.

To illustrate that it would have been possible to have twins beginning to form at 98.2% reduction, Figure 4 shows a specimen cut from sample Z before it underwent heat treatment. It indicates the beginning of cubical alignment in the specimen. Cubical alignment may indicate the presence of twins.(11) Therefore, it must be assumed that the increase in the per cent reduction in Z over Y caused twins to form which promoted secondary recrystallization.

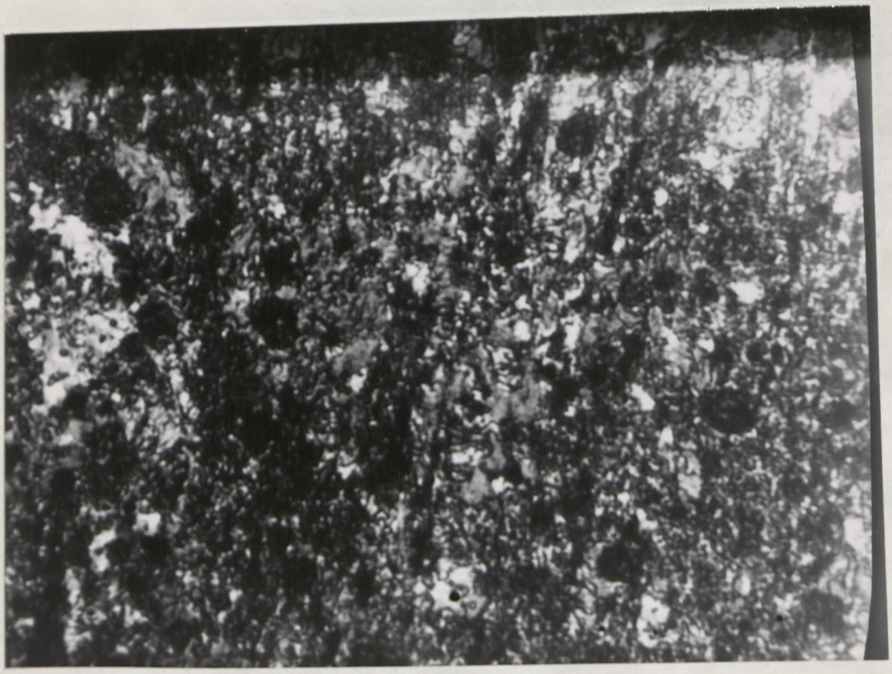

Figure 4. A Photomicrograph of Sample Z Before Heat Treatment (The cubically-aligned structure is in the center and runs nearly vertical). Magnification 240x

An example of secondary recrystallization is shown in Figure 5. To prepare the specimen for photography, it was etched in the usual manner, and then it was etched with an equal mixture of ammonium hydroxide, hydrogen peroxide, and water. The actual size of the grains in the specimen can be estimated by using the rule in the photograph. This rule is graduated in tenths-of-inches.

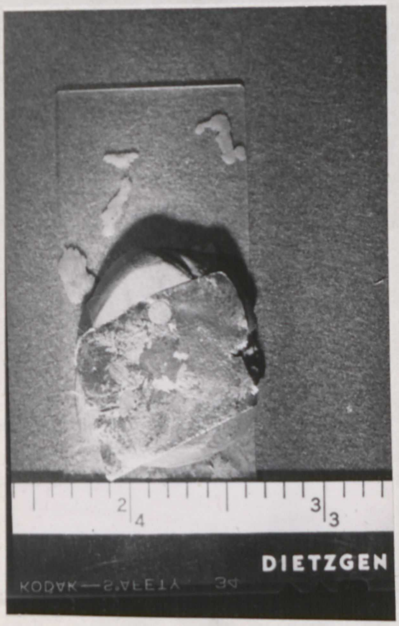

Figure 5. A Photograph of Sample Z After Secondary Recrystallization Had Occurred. (Actual Size)

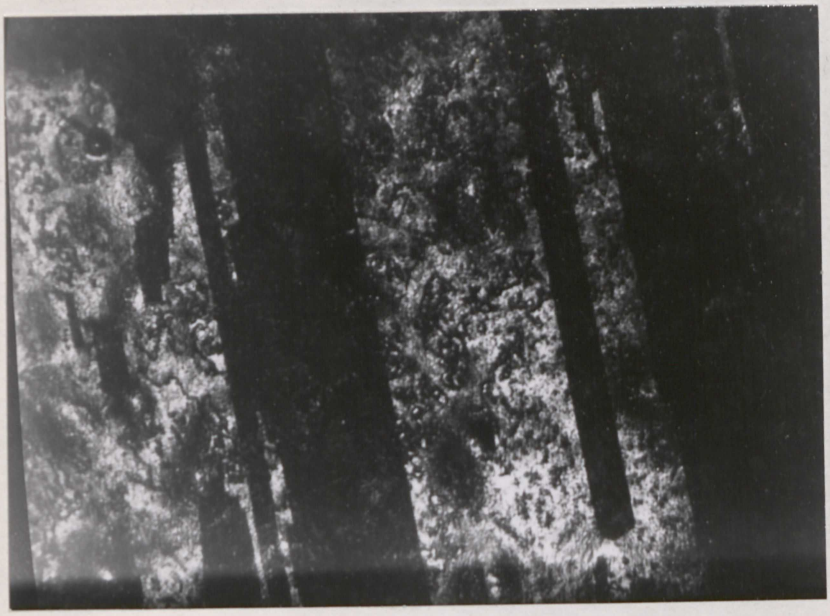

Figure 6. A Photomicrograph of Sample Z Showing the Twinned Structure. Magnification 150x

Another photomicrograph is shown in Figure 6. This sample shows the twinned structure present in sample Z after secondary recrystallization had occurred. Kronberg and Wilson found in their experimental observations that twin boundaries would not disappear, but would just be reoriented after secondary recrystallization occurred.(11)

CONCLUSIONS AND RECOMMENDATIONS

Secondary recrystallization occurred in copper reduced 98.2% with a heat treatment of 48 hours at 1890° F., but did not occur with the same heat treatment for a reduction of 97%. This result is in conflict with Guido, who found secondary recrystallization to occur in copper after a 90% reduction at a temperature of 1832° F.(8) and with Cooke and Richards, who found secondary recrystallization to occur after a 97% reduction with a heat treatment of one hour at 1832° F., but Cooke and Richards used a straight-roll method to achieve their reduction(6) and Guido used copper wire for his specimens.(8) The method used to achieve the reductions necessary for samples Y and Z was a combination of compression-roll and straight-roll reductions.

A completely compression-rolled series of specimens was tested by Bowles and Boas at a temperature of 1860° F. for one hour, and they found that a reduction of 98.6% by compression-rolling was necessary before secondary recrystallization occurred.(3) Since it was impossible to prepare samples by complete compression-rolling or straight-rolling methods in the laboratory, these previous investigations(3, 6, 8) must be assumed correct if any analysis of the results is to be made.

From the experimental results given in Table I, it can only be assumed that the compression reduction of 71.5% used in the preparation of samples U, T, Y, Z, and AA, increased the per cent reduction necessary to promote secondary recrystallization up to 98.2%. To confirm this conclusion, a series of tests should have been run under the same conditions as those used in the tests of samples Y and Z, but furnace construction limited these tests. The reason that the furnace was a limiting factor was that the glass tube softened at about 1720° F., and it was useless after the 1890° F. test was complete.

It can easily be seen from the preceding paragraph that further work could be carried out on this subject of secondary recrystallization. To aid in this work, the glass tube in the furnace could be replaced by a quartz tube which would permit a higher operating temperature than 1720° F. Then tests could be run on samples that had undergone different degrees of compression rolling before straight rolling was begun. For each different compression-rolled specimen, samples ranging from 93 to 99% reduction should be prepared. If it were possible, a series of completely compression-rolled samples and a series of completely straight-rolled samples should be prepared. Then, a more complete answer to the effect of partial compression-rolling on secondary recrystallization could be obtained.

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