RECOVERY AND RECRYSTALLIZATION OF U_3Si

by

P.F. Caillibot* and B.S. Wyatt

ABSTRACT

The recovery and recrystallization temperatures of U_3Si were determined for an alloy of uranium-3.98 wt% silicon containing 600 ppm carbon. Small specimens, deformed by compression, were isothermally and isochronally annealed at temperatures between 350 and 700°C and their recovery and recrystallization temperatures determined using hardness, grain size and X-ray measurements. For small amounts of strain and an annealing time of 6 hours both recovery and recrystallization begin at 400-450°C. Complete recrystallization is achieved at 650-700°C.

The effect of small changes in silicon and carbon concentration were determined by examining two further alloys containing 3.27 wt% silicon and 600 ppm carbon, and 4.02 wt% silicon and 140 ppm carbon respectively. A small change in silicon concentration does not affect recovery and recrystallization but decreasing the carbon concentration from 600 to 140 ppm decreases the recovery and recrystallization temperatures.

AECL-3472

Chalk River Nuclear Laboratories
Fuel Materials Branch
October, 1969

*Summer student from École Polytechnique, Montreal, now with Hydro Quebec.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Récupération et recristallisation de l'U_3Si

par P.F. Caillibot* et B.S. Wyatt

*Etudiant de l'Ecole polytechnique à Montréal ayant travaillé l'été à Chalk River, maintenant à la Commission électrique du Québec.

Résumé

Les températures de récupération et de recristallisation de l'U_3Si ont été déterminées pour un alliage d'uranium-silicium (3.98% en poids) contenant 600 ppm de carbone. De petits échantillons déformés par compression, ont été isothermiquement et isochroniquement recuits à des températures se situant entre 350 et 700°C et leurs températures de récupération et de recristallisation déterminées au moyen de mesures basées sur la dureté, la dimension des grains ou au moyen de rayons X. Pour de petites contraintes et pour une durée de recuit de 6 heures, la récupération et la recristallisation commencent à 400-450°C. Une recristallisation complète est obtenue à 650-700°C.

L'effet de petits changements dans la concentration du silicium et du carbone a été déterminé en examinant deux autres alliages contenant l'un 3.27% en poids de silicium et 600 ppm de carbone et l'autre 4.02% en poids de silicium et 140 ppm de carbone. Une petite modification dans la concentration du silicium ne nuit pas à la récupération et la recristallisation mais si l'on fait passer la concentration de carbone de 600 à 140 ppm on réduit les températures de récupération et de recristallisation.

L'Energie Atomique du Canada, Limitée

Chalk River, Ontario

Octobre 1969

AECL-3472

1. INTRODUCTION

The amount of published information on the physical, mechanical and thermal properties of U_3Si is very limited when compared with other nuclear fuels such as uranium metal. As far as is known there has been no previous attempt to study the effect of deformation followed by exposure to temperatures similar to those U_3Si will experience when used as a nuclear fuel, i.e. 400-650°C. A knowledge of whether U_3Si will recrystallize at these temperatures may help in determining the mechanism(s) responsible for the irradiation swelling that occurs at low burnup[1,2,3,4].

This report describes measurements of recovery and recrystallization temperatures of U_3Si and the effects of small changes in silicon and carbon concentrations on these temperatures. The amount of room temperature deformation that the U_3Si could withstand under compression, without fracture, was only sufficient to produce a 10% reduction in height. The recovery and recrystallization temperatures are determined, therefore, for small amounts of strain.

2. EXPERIMENTAL

2.1 Preparation of Material

Material was obtained from Eldorado Nuclear Limited in the form of cast bars 16 mm diameter x 150 mm long. The bars were heat treated, under a vacuum of 5×10^{-6} Torr, for 72 hours at 800°C to transform the as-cast structure to the δ-phase (U_3Si). Most of the investigation was carried out on a single alloy (heat 319) containing 3.98 wt% silicon and 600 ppm carbon. The effects of small changes in silicon and carbon concentrations were studied by carrying out a number of tests on two further alloys:

1) Heat 313 containing 3.27 wt% silicon and 600 ppm carbon.

2) Heat 300 containing 4.02 wt% silicon and 14 ppm carbon.

A typical as-cast structure is shown in Figure 1. The structures of the three alloys after heat treatment,

a) etched in Murakami's reagent to show the phases present and

b) etched in a grain boundary etch[5] to reveal the grain structure of the U_3Si

are shown in Figures 2-7. The average grain size of the U_3Si and hardness of the three alloys were:

Heat 319 - 9.6 μm - 263 VPN

Heat 313 - 8.0 μm - 251 VPN

Heat 300 - 8.25 μm - 267 VPN

2.2 Compression Tests

Attempts to cold work the alloys in tension were not successful so small parallelepipeds about 11 mm long and with a square cross-section, of about 30 mm^2, were cut from the U_3Si rods and cold worked by compression in a 10 tons press.

A stress strain curve was plotted using the true compressive stress[6,7] and the reduction in height of the specimens (Figure 8). The true strain[6,7] was also calculated and is included for reference.

2.3 Annealing of Cold Worked Samples

The cold worked specimens were sectioned through the centre and sealed in quartz capsules under a vacuum of 5×10^{-6} Torr. Specimens from heat 319 were annealed isothermally at 400, 500 and 600°C for periods of time up to 50 hours. In view of the results obtained it was decided to isochronally anneal specimens of all three alloys for 6 hours at temperatures between 350 and 700°C. After annealing, all specimens were quenched into cold water.

2.4 Determination of Grain Size

The average grain diameter (d μm) of the U_3Si was determined on all the isochronally annealed specimens from the formula:

$$d = \left[\frac{A}{N} \times \frac{1}{(1000)^2} \times 10^8 \left(\frac{100-P}{P}\right)\right]^{\frac{1}{2}}$$

where A = Area examined (in sq cms) at a magnification of 1000X,

N = Number of grains in area A,

P = Percentage of UO_2, U_3Si_2, free uranium and voids in area A (determined by an intercept method).

2.5 Hardness Determinations

The Vickers hardness numbers (VPN) were determined on all of the isochronally and isothermally annealed specimens. The hardnesses were determined on a polished and etched face using a 30 kg load. Determinations were done in triplicate on all specimens.

2.6 X-Ray Measurements

Back reflection X-ray photographs were taken on all specimens from heat 319 that had been isochronally annealed. The width of the peak for the (202) Bragg X-ray reflection was measured at half the peak height in order to follow recrystallization[8,9]. However only the readings from the specimens cold worked 10% were used because the small amount of strain in the other specimens made difference in peak width difficult to measure.

3. RESULTS

3.1 Isothermal Anneals

The hardness of specimens of heat 319 cold worked to a reduction in height of 7% and isothermally annealed at 400, 500 and 600°C are plotted against annealing time in Figure 9. The specimens annealed at 400 and 500°C had not returned to the fully annealed hardness after 50 hours at temperature, whereas the specimens annealed at 600°C had very nearly returned to their fully annealed hardness in about 6 hours. Owing to this low level of cold work, which had not obviously deformed the original grains, the identification of new recrystallized grains by metallographic inspection was uncertain. Very small grains were visible, mainly in the vicinity of residual U_3Si_2 particles, but these were also seen in the structure before the specimens were cold worked.

3.2 Isochronal Anneals

The hardness of specimens of heat 319 cold worked 3, 7 and 10% and isochronally annealed for 6 hours at temperatures between 400 and 700°C are plotted against temperature in Figure 10. All the specimens annealed at temperatures >600°C appear to have fully recovered irrespective of the degree of cold work.

The grain sizes of the same specimens are plotted against temperature in Figure 11. A drop in grain size occurs as the annealing temperature is raised, the minimum grain size occurring at different temperatures depending on the amount of prior cold work. Eventually grain growth begins and the grain size increases to a size greater than the initial value of 9.6 μm, (Figure 12).

Figure 13 shows a plot of the (202) Bragg X-ray reflection peak width versus annealing temperature for specimens of heat 319 cold worked 10%. Complete removal of the effects of cold work does not appear to have been achieved at temperatures up to 700°C.

3.3 Effect of Silicon Concentration

The hardnesses of specimens from heat 313 (3.27 wt% Si, 600 ppm C), cold worked 3, 7 and 10% and isochronally annealed 6 hours at temperatures between 400 and 700°C are plotted against temperature in Figure 14. The specimens cold worked 3 and 10% appear to have recovered fully after 6 hours at 700°C but the specimens cold worked 7% are still somewhat harder (265 VPN) than the fully annealed value (251 VPN).

Figure 15 shows a plot of the grain size of specimens from heat 313 versus annealing temperature. The relationship between grain size and annealing temperature is very similar to that observed for heat 319; an initial drop in grain size followed by grain growth as the annealing temperature is increased.

3.4 Effect of Carbon Concentration

The hardness versus annealing temperature curves for heat 300 (4.02 wt% Si, 140 ppm C) cold worked 3, 7 and 10% are shown in Figure 16. The specimens cold worked 3 and 7% appear to have fully recovered to their original hardness at temperatures just below 600°C, while those cold worked 10% have fully recovered at a slightly higher temperature.

The grain sizes for these specimens are plotted against annealing temperature in Figure 17. Grain growth appears to have begun even at 400°C. There is no sign of an initial fall in grain size as in the previous two alloys.

4. DISCUSSION

4.1 Recovery and Recrystallization of Heat 319

The curves in Figure 9 for specimens isothermally annealed at 500 and 600°C are characteristic of those showing recovery of mechanical properties. The rate of decrease of hardness starts rapidly and then proceeds at a slower and slower rate as the driving force is expended.

Initiation of hardness recovery is delayed in the specimens annealed at 400°C but the same effect as above is apparent after about 5-10 hours at temperature. The driving force for the reaction does not appear to be sufficient, however, to produce complete hardness recovery at 400 and 500°C. The curves in Figure 10 show that hardness recovery commences below 400°C in specimens cold worked 10% but complete recovery is not obtained below about 600°C.

There is no direct metallographic evidence for new recrystallized grains having formed during annealing. Figure 11, however, suggests that new grains must have nucleated because there is a significant drop in grain size as the annealing temperature is increased. From this evidence, it appears that recrystallization begins at 400-450°C for a 6 hour anneal in specimens cold worked 10%. For the same specimens, recovery and/or recrystallization, as measured by decrease in line broadening due to cold work[8,9], begins at about 450°C (Figure 13). The curves in Figures 10 and 11 suggest that recovery and recrystallization are complete after a 6 hour anneal at temperatures between 650 and 700°C.

For specimens cold worked 3 and 10% the effect of cold work on the recovery and recrystallization is that observed in most materials, i.e. an increase in cold work decreases the temperatures at which recovery and recrystallization occurs. The specimens cold worked 7% are however slightly anomalous in that the temperatures at which the grain size decreases appear to be lower than those for the specimens cold worked 10%. Recovery of hardness in the 7% cold worked specimens, however, closely follows that in the 3% cold worked specimens.

4.2 Effect of Silicon Concentration

Figures 14 and 15 give temperatures of 400-450°C for commencement of recovery and recrystallization, and 650-700°C for their completion, in material of heat 313 (3.27 wt% Si) cold worked 10%. These temperatures are the same as those found for heat 319, having a silicon content of 3.98 wt% silicon. The curves relating hardness and grain size with annealing temperature (Figures 18 and 19) are very similar for both alloys; the higher overall hardness of heat 319 can be attributed to its higher silicon concentration. It does not appear therefore that small variations in silicon concentration significantly affect the recovery and recrystallization temperatures of U_3Si.

4.3 Effect of Carbon Concentration

Examination of Figures 9 and 16 shows that recovery occurs at a much lower temperature in specimens from heat 300 (4.02 wt% Si, 140 ppm C) than for specimens from heat 319. We estimate from Figure 16 that recovery begins at a temperature below 350°C for all cold worked specimens from heat 300, and is completed between 550 and 600°C. The curves relating annealing temperature to grain size for specimens from heat 300 (Figure 17) suggest that either recrystallization does not occur or it occurs below 350°C, the minimum temperature studied. No decrease in average grain size with increasing annealing temperature was seen in this alloy such as was seen in the two alloys containing greater amounts of carbon. Corresponding hardness recovery and grain size curves for all three alloys are compared in Figures 18 and 19.

A small increase in the carbon level (140 ppm - 600 ppm) does not appear to have a significant effect on hardness recovery of U_3Si when deformations are relatively high (10% CW), but for low deformations (3 and 7% CW) the increase definitely retards recovery (compare Figures 10 and 16). A possible explanation is that carbon finely dispersed in the U_3Si as a carbide[10] has a pinning effect on the dislocation network, reducing the rate of recovery at lower temperatures. This appears to be borne out by the results of isothermally annealing an alloy with 600 ppm at 400°C (Figure 9). The more cold work the alloy receives, the greater the amount of stored energy available to overcome the pinning effect, so that at the 10% cold work level it is possible to compensate for the relatively small amount of additional carbon.

4.4 Grain Growth

The presence of a uniform distribution of a coarse second phase, either U_3Si_2, uranium or UO_2 inclusions, in most U_3Si alloys, presumably restrains grain growth. Most of these dispersed particles are at the U_3Si grain boundaries (Figures 3, 5 and 7).

Increasing the carbon level from 140 to 600 ppm appears to restrain grain growth irrespective of the amount of deformation or annealing temperature. In Figure 19 it can be seen that in heat 300, containing only 140 ppm carbon, grain growth occurs at 350°C whereas in the higher (600 ppm) carbon alloy, heat 319, grain growth does not begin until temperatures as high as 500-550°C have been reached.

Carbon, being less soluble in U_3Si than U_3Si_2, is precipitated as uranium carbide in the U_3Si matrix surrounding residual U_3Si_2 particles when the as-cast alloy is initially transformed. Such a dispersion of carbide might pin grain boundaries sweeping through the U_3Si matrix. At higher temperatures, both the mobility of the carbon atoms in the matrix and the ability of the grain boundaries to unpin themselves increases, permitting grain growth to proceed.

The proposed effect of carbon on grain growth is consistent with the observation that small U_3Si grains are segregated adjacent to U_3Si particles in the matrix, where the maximum concentration of carbon is expected to occur.

5. CONCLUSIONS

- Recovery, as measured by hardness and by X-ray line broadening measurements, begins at 400-450°C is is complete after 6 hours at 650-700°C in an alloy containing 3.98 wt% Si and 600 ppm carbon, cold worked 10%.

- Although recrystallisation was not directly observed metallographically, measurements of average grain size in the same alloy are consistent with concurrent processes of recovery and recrystallization.

- No effect on recovery or recrystallization was produced by a change in silicon concentration from 3.98 to 3.27 wt%.

- A decrease in carbon concentration from 600 to 140 ppm decreased the recovery temperature and increased the rate of grain growth at lower temperatures. The effect of carbon is attributed to the pinning of grain boundaries by uranium carbide inclusions in the U_3Si.

6. REFERENCES

1) Bleiberg, M.L. and Jones, L.J., "The Effects of Pile Irradiation on U_3Si". WAPD-T-497 (1957).

2) Howe, L.M., "Irradiation Behaviour of Enriched U_3Si Elements Sheathed in Zircaloy-2". AECL-984 (January 1960).

3) Kittel, J.H. and Smith, K.F., "Effects of Irradiation on Some Corrosion Resistant Fuel Alloys". ANL-5640 (May 1960).

4) Feraday, M.A., Chalder, G.H. and Cotnam, K.D., "Irradiation Behaviour of Cored U_3Si Fuel Elements". Nuclear Applications, Vol. 4 (March 1968).

5) Ambler, J.F.R. Private Communication to Wyatt, B.S.

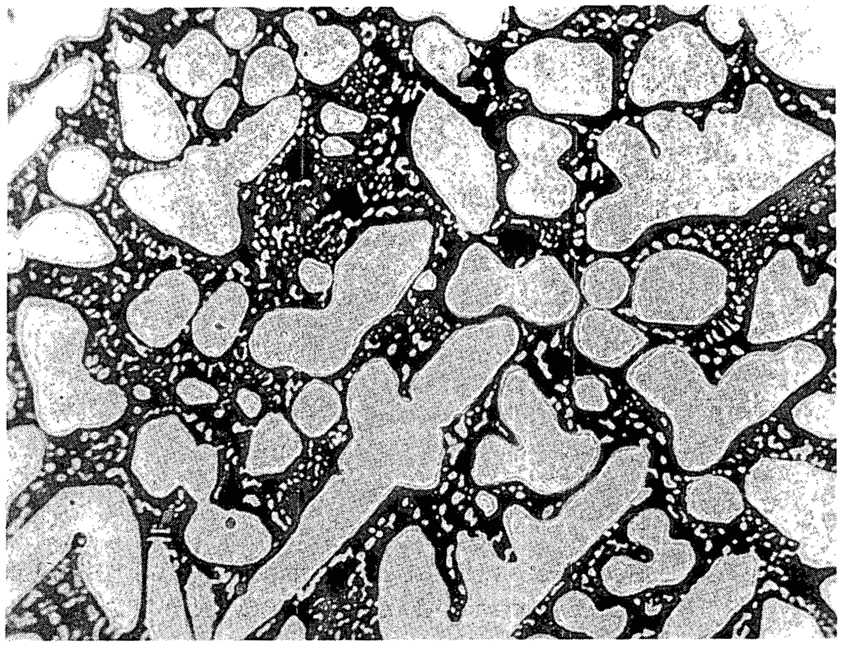
6) Hockett, J.E., "True Strain Rate Compression Testing in a CAM Plastometer". Metal Progress, Vol. 91, No. 6 (June 1967).

7) Dieter, A.E., "Mechanical Metallurgy", McGraw Hill Book Co. Inc. (1961).

8) Chalmers, B. and Quarrell, A.G., "The Physical Examination of Metals", 2nd Ed., p.308, Edward Arnold (Publishers) Ltd. (1960).

9) Taylor, A., "X-Ray Metallography", p.269, John Wiley & Sons, New York (1961).

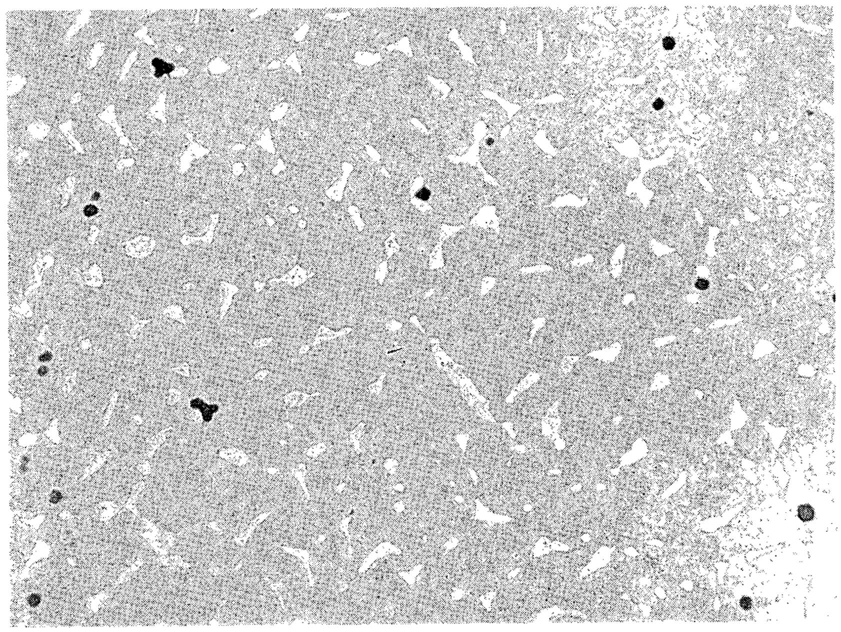
10) Guinet, P., Vaugoyeau, H., Langier, J. et Blum, P.L., "Étude d'un équilibre à 4 phases solides dans le système ternaire U-C-Si". J. Nuclear Materials 21 p.21-31 (1967).



Met J151 C2 X500

Figure 1 Typical As-Cast Structure

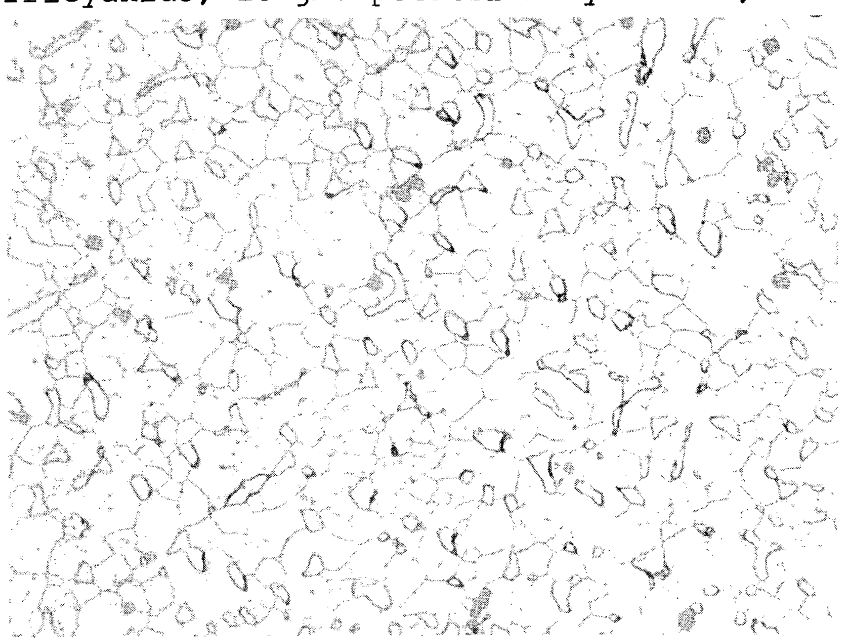
Primary U_3Si_2 (white) surrounded by a rim of U_3Si (grey). Dark matrix is uranium containing small grey particles of U_3Si formed from the original eutectic during cooling.



Met J151 F1 X500

Figure 2 Sample 319, Uranium-3.98 wt% Silicon
Heat Treated at 800°C for 72 Hours

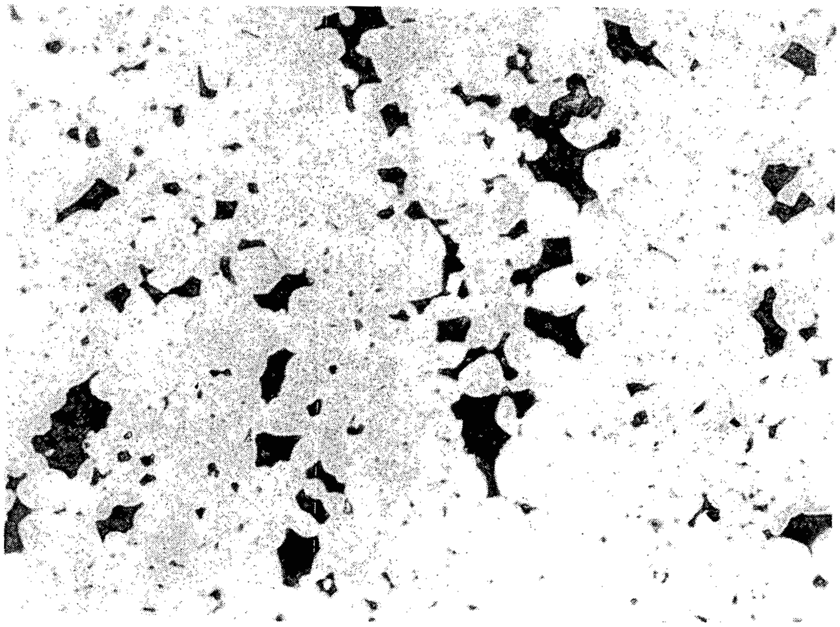
Grey matrix - U_3Si, white particles - U_3Si_2, black particles - porosity or UO_2 etched in Murakami's reagent. (10 gms potassium ferricyanide, 10 gms potassium hydroxide, 100 ccs H_2O)



Met J151 F2 X500

Figure 3 Same Alloy as in Figure 2

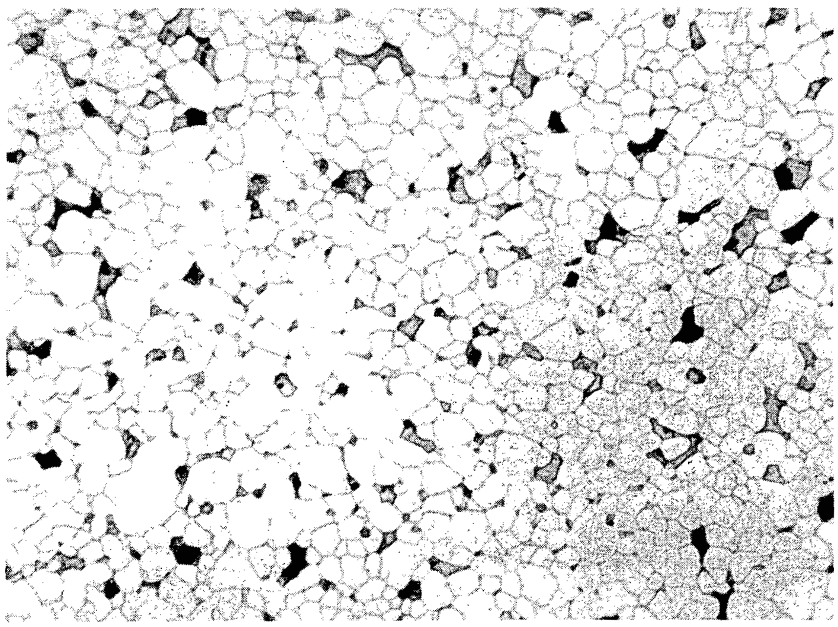
Etched to show grain boundaries (3.4 gms citric acid, 72 ccs nitric acid, 1 cc 48% hydrofluoric acid, 170 ccs H_3O).



Met J151 G1 X500

Figure 4 Sample 313, Uranium-3.27 wt% Silicon, Heat Treated at 800°C for 72 Hours

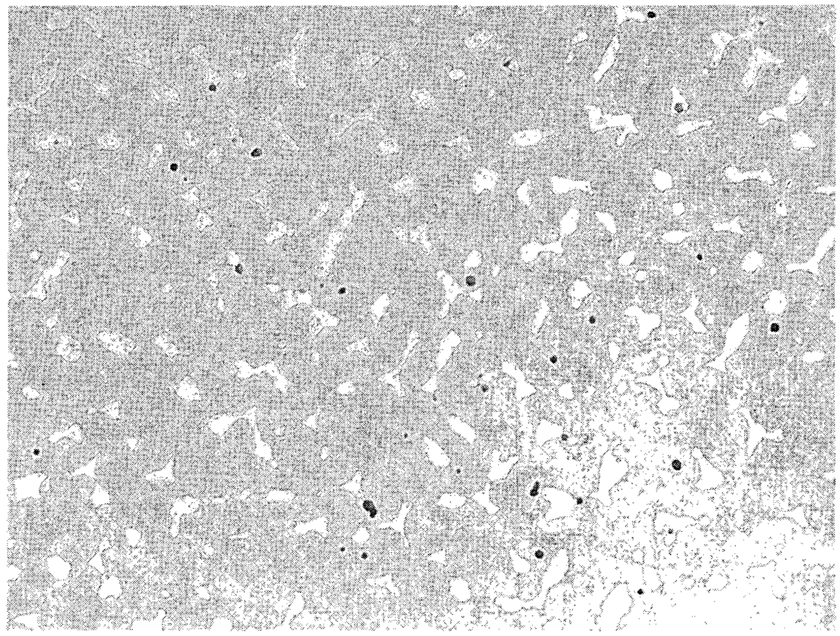
Grey matrix - U_3Si, dark phase - uranium, etched in Murakami's reagent.



Met J151 G2 X500

Figure 5 Same Alloy as in Figure 4

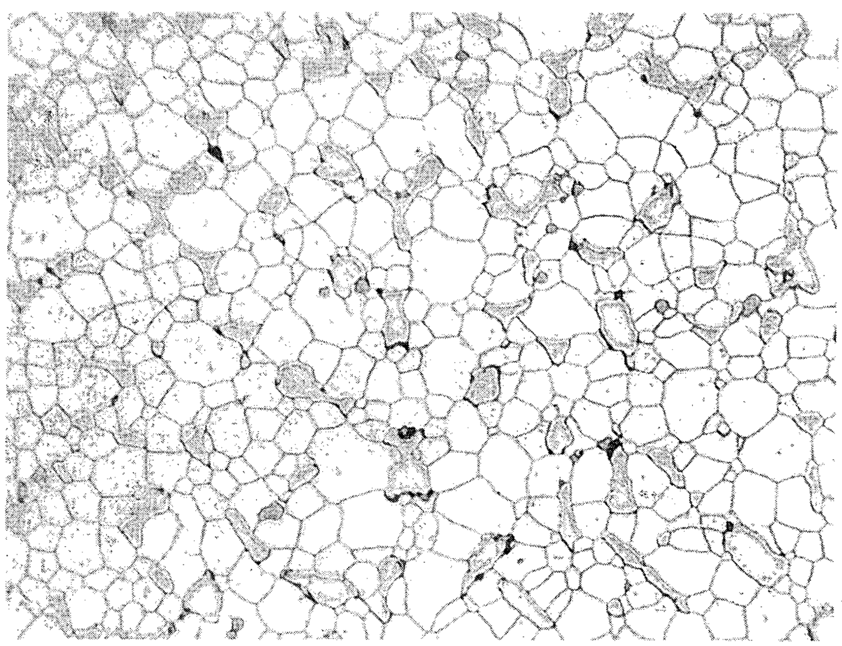
Etched to show grain boundaries.



MET J151 E1 X500

Figure 6 Sample 300, Uranium 4.02 wt% Silicon Heat Treated at 800°C for 72 Hours

Grey matrix - U_3Si, white particles - U_3Si_2, black particles - porosity or UO_2 etched in Murakami's reagent.



MET J151 E2 X500

Figure 7 Same Alloy as in Figure 6

Etched to show grain boundaries.

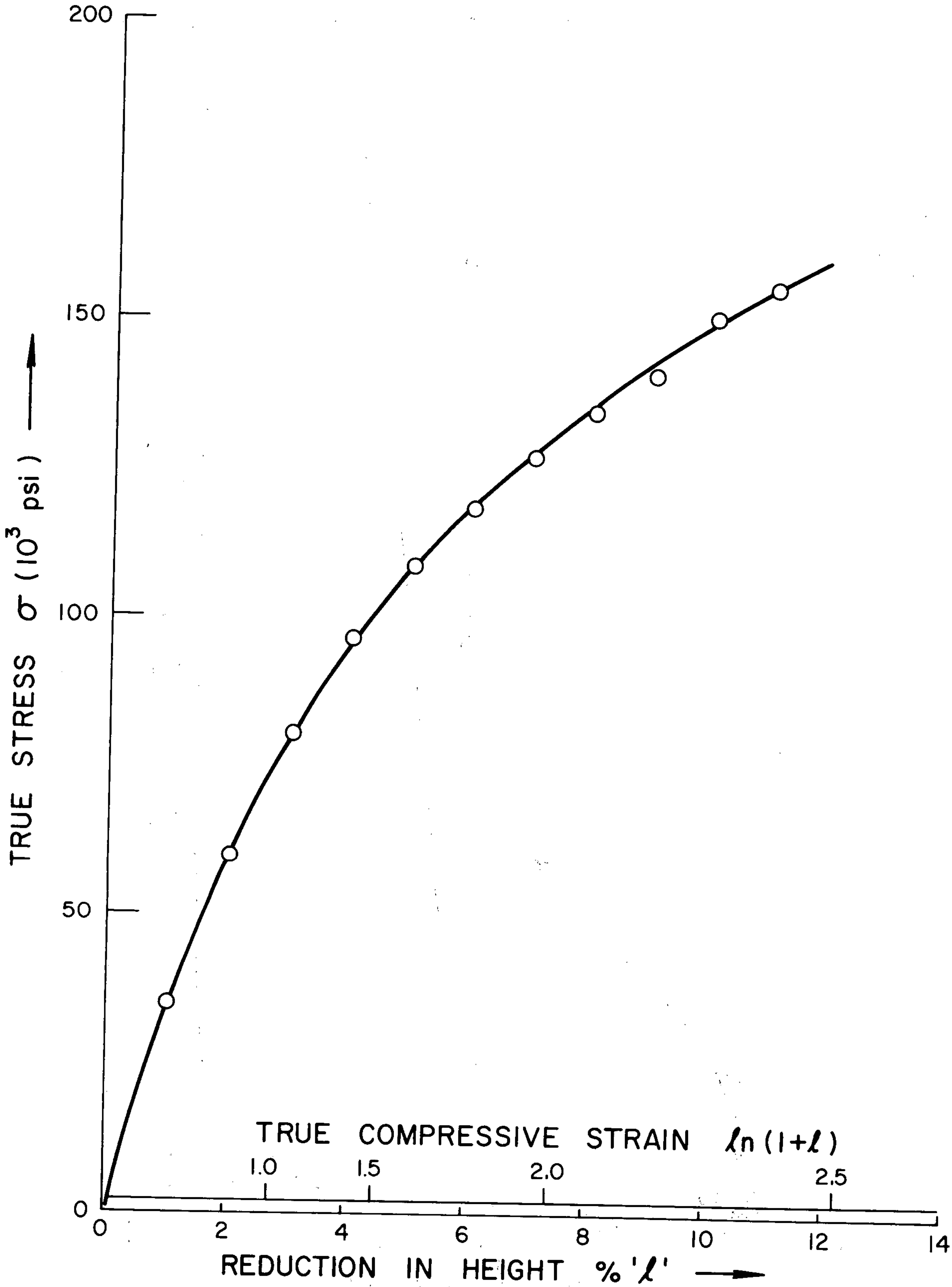


Figure 8

Stress-strain curve for U_3Si parallelepipeds deformed under compression.

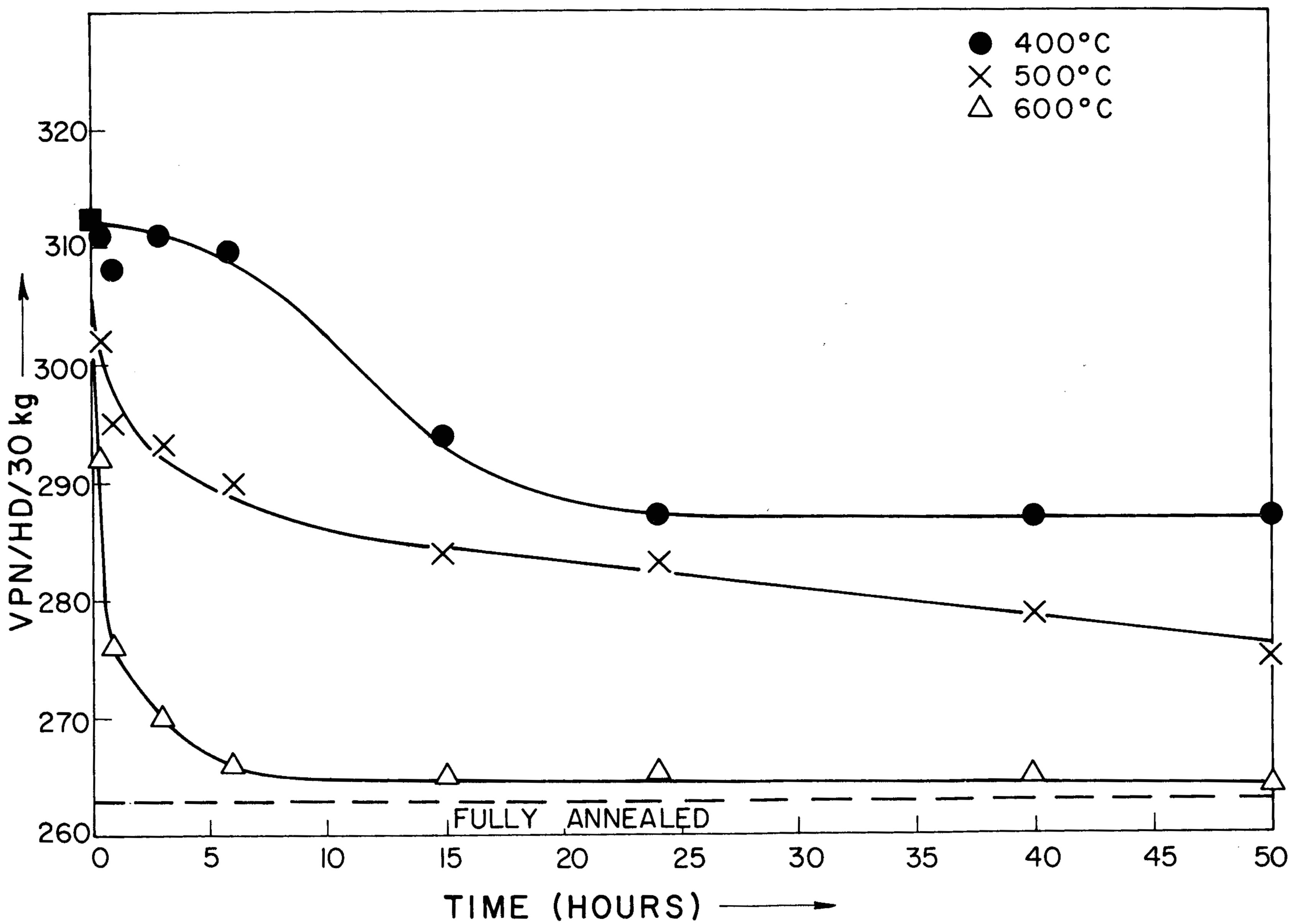


Figure 9

Change in hardness with time at three annealing temperatures. Sample 319 (3.98 wt% Si, 600 ppm C) cold worked 7%.

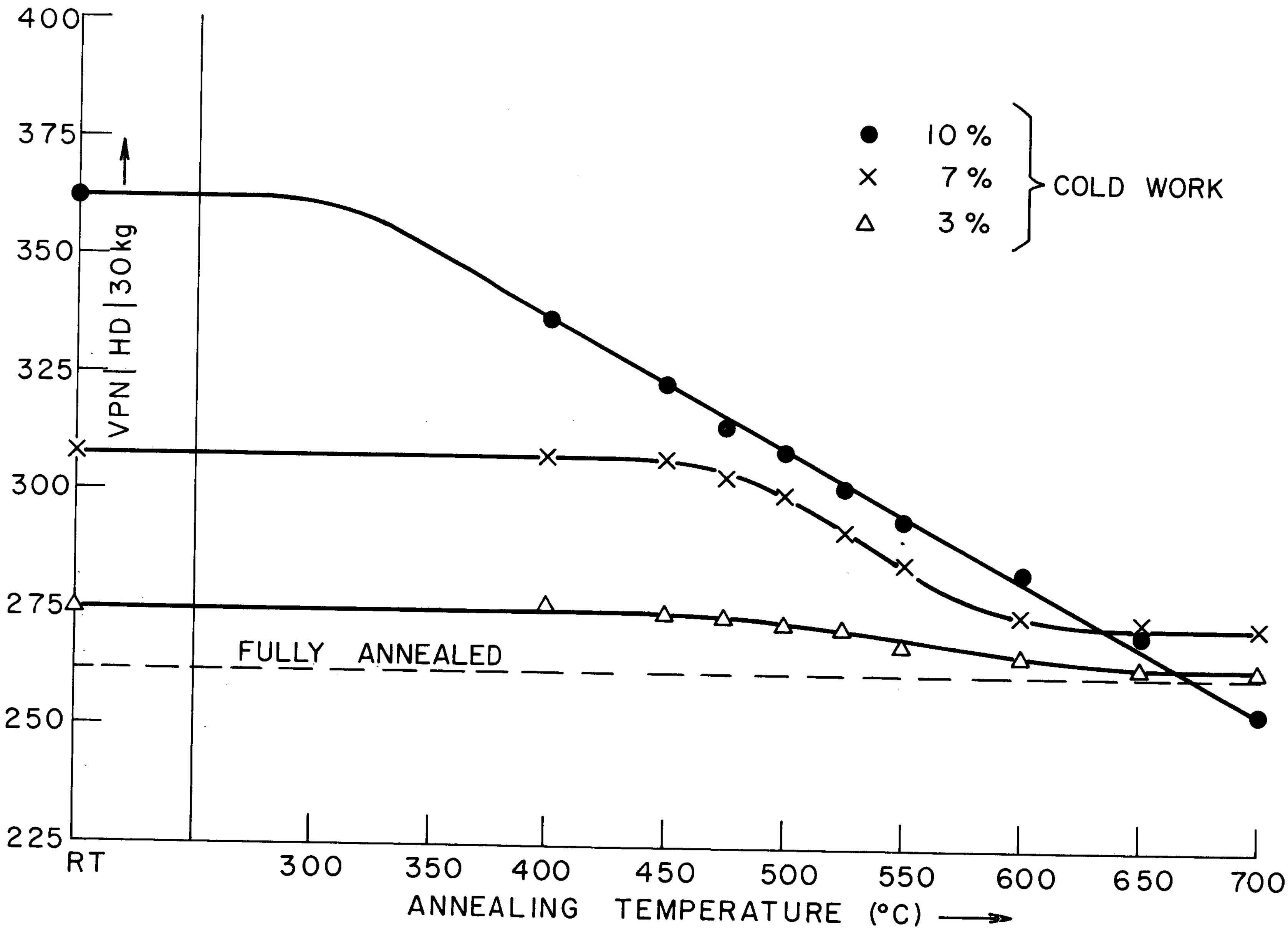


Figure 10

Change in hardness with annealing temperature. Sample 319 (3.98 wt% Si, 600 ppm C).

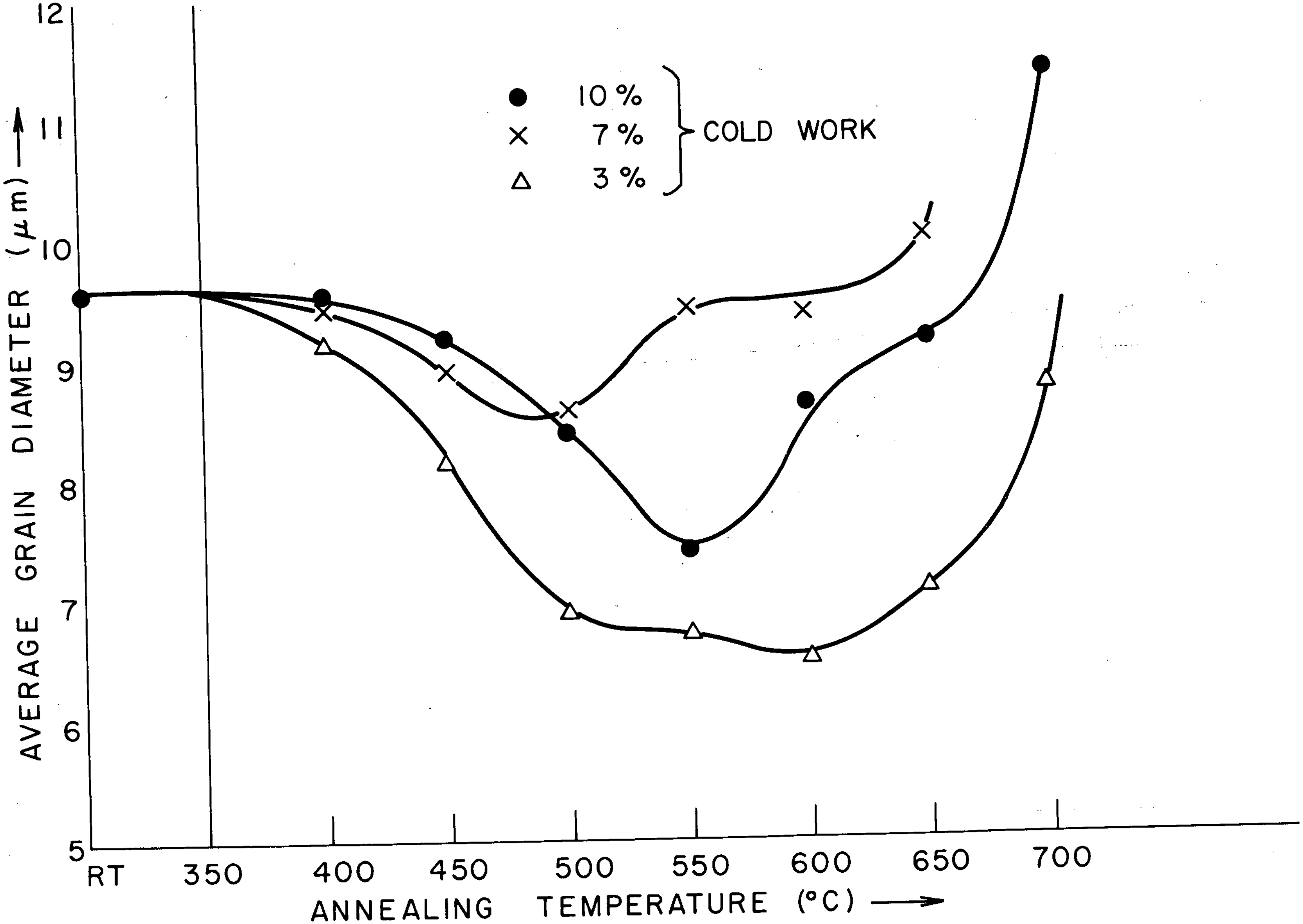
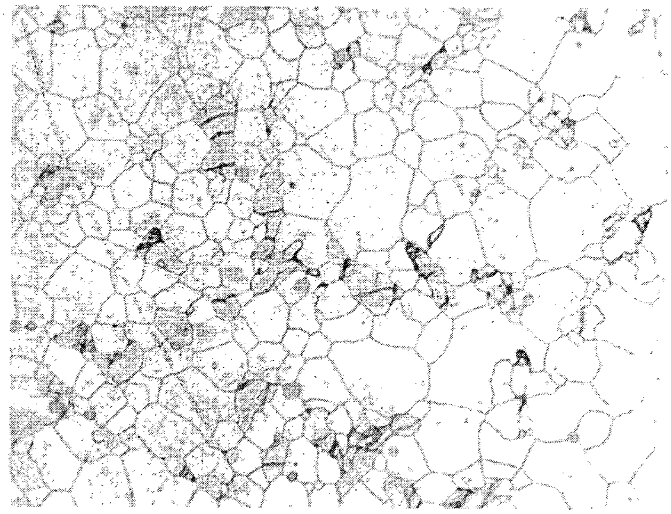
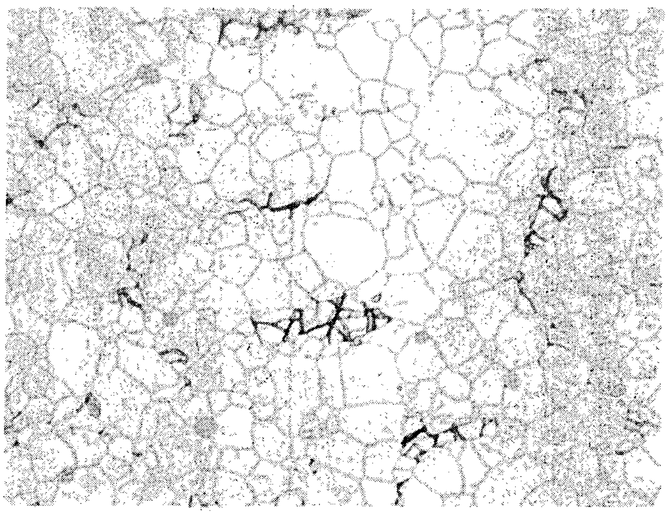


Figure 11
Change in average grain size with annealing temperature. Sample 319 (3.98 wt% Si, 600 ppm C).

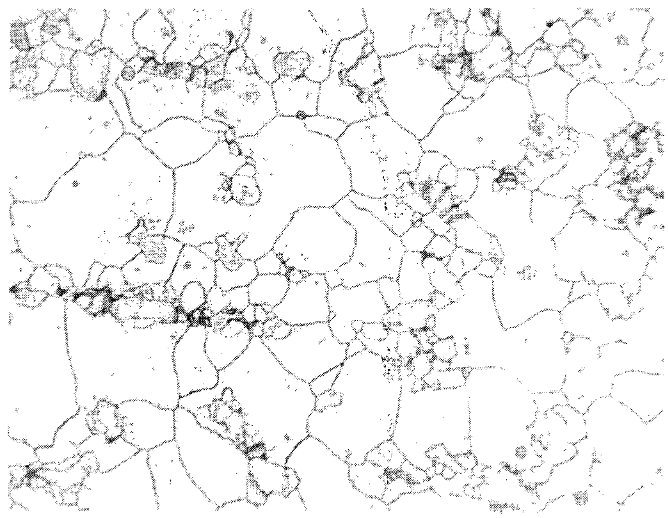
MET J190 D1 A X500



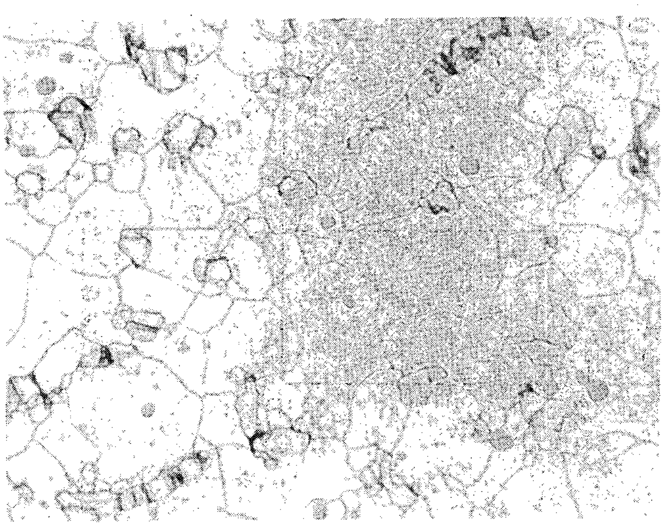
MET J190 B1 B X500



MET J190 C1 C X500



MET J190 A1 D X500



MET J190 E1 E X500

Figure 12 Sample 319, Cold Worked 10%, Annealed 6 Hours at:

A - 500°C

B - 550°C

C - 600°C

D - 650°C

E - 700°C

Etched to show grain boundaries.

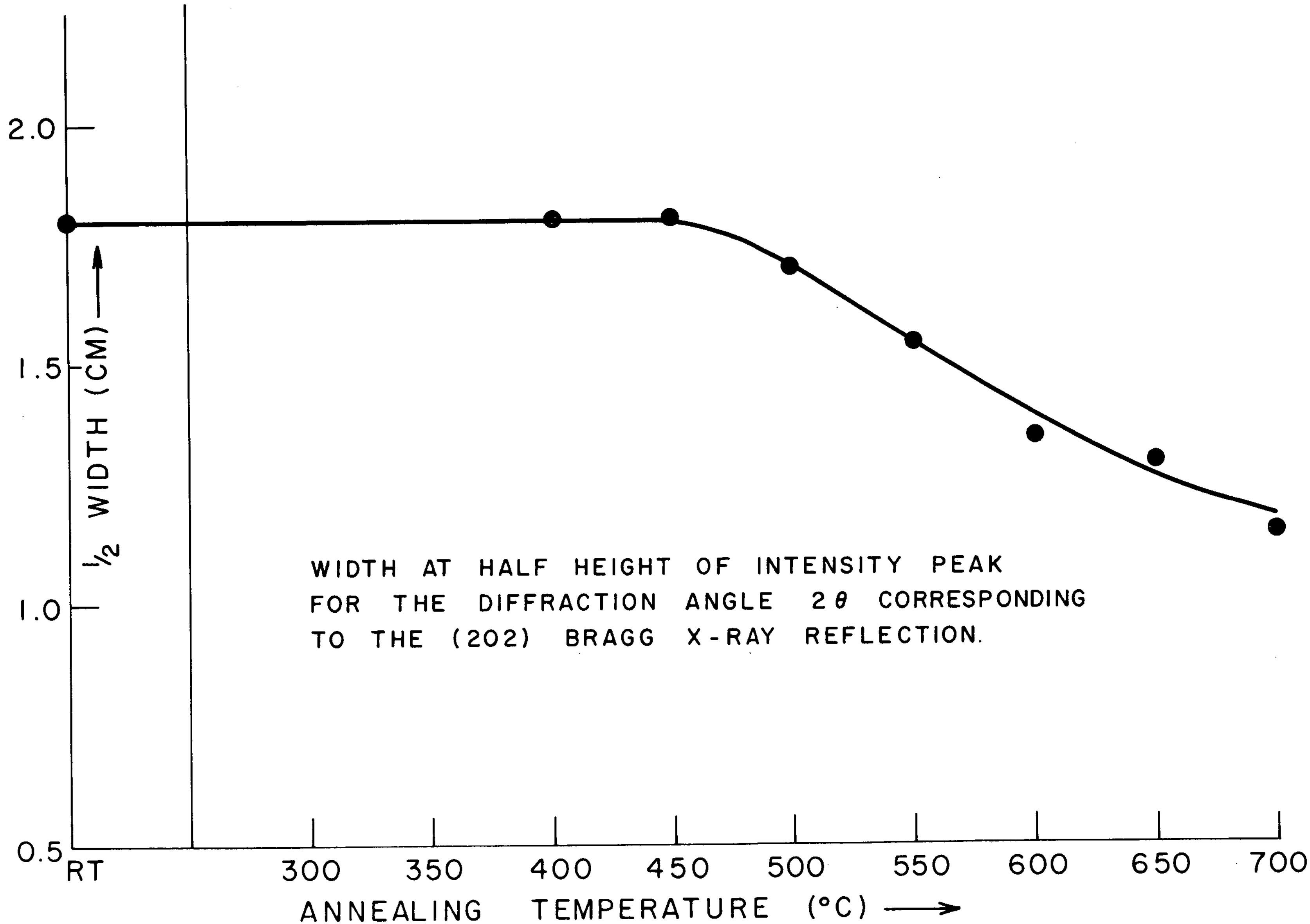


Figure 13

Effect of annealing temperature on X-ray line broadening. Sample 319 (3.98 wt% Si, 600 ppm).

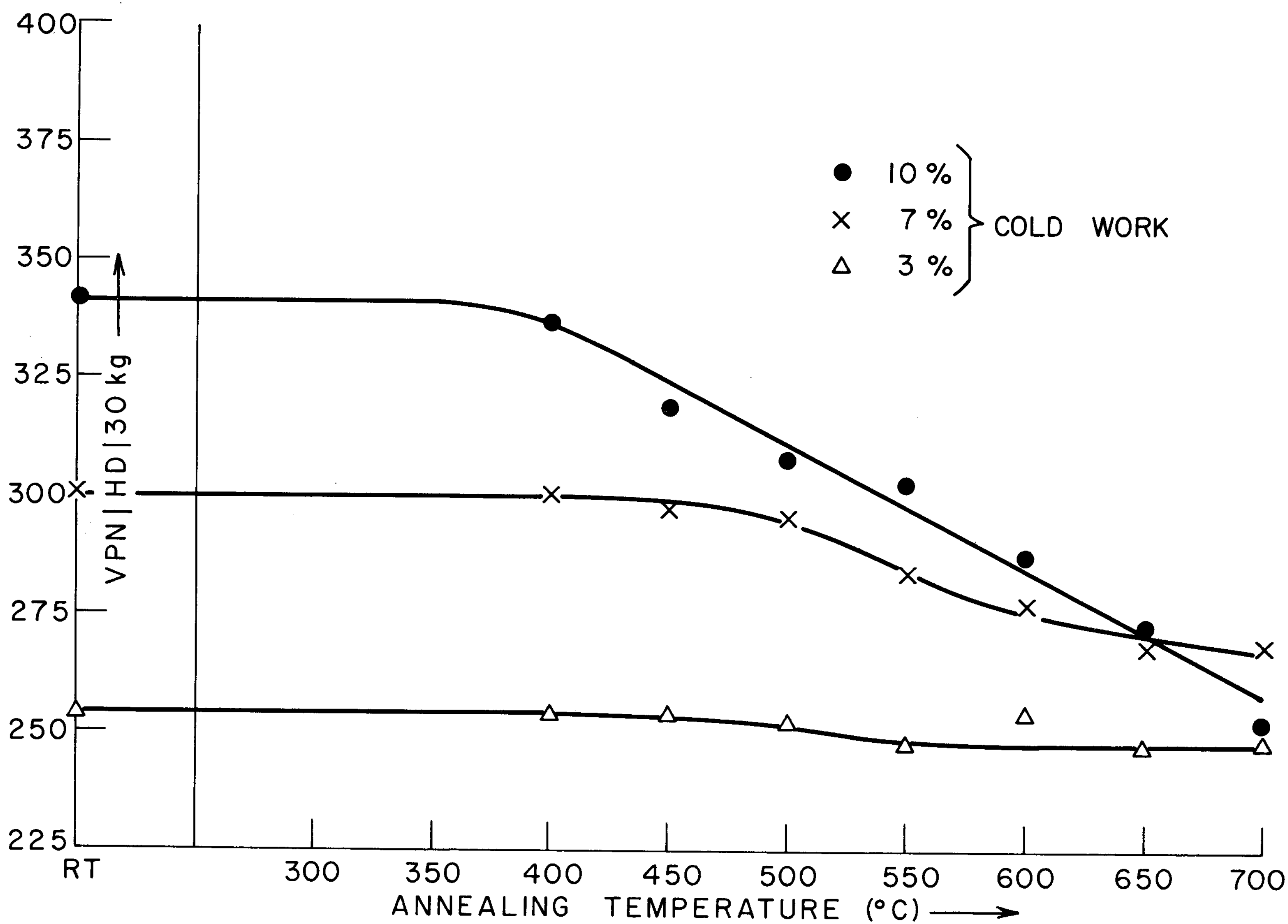


Figure 14

Change in hardness with annealing temperature. Sample 313 (3.27 wt% Si, 600 ppm C).

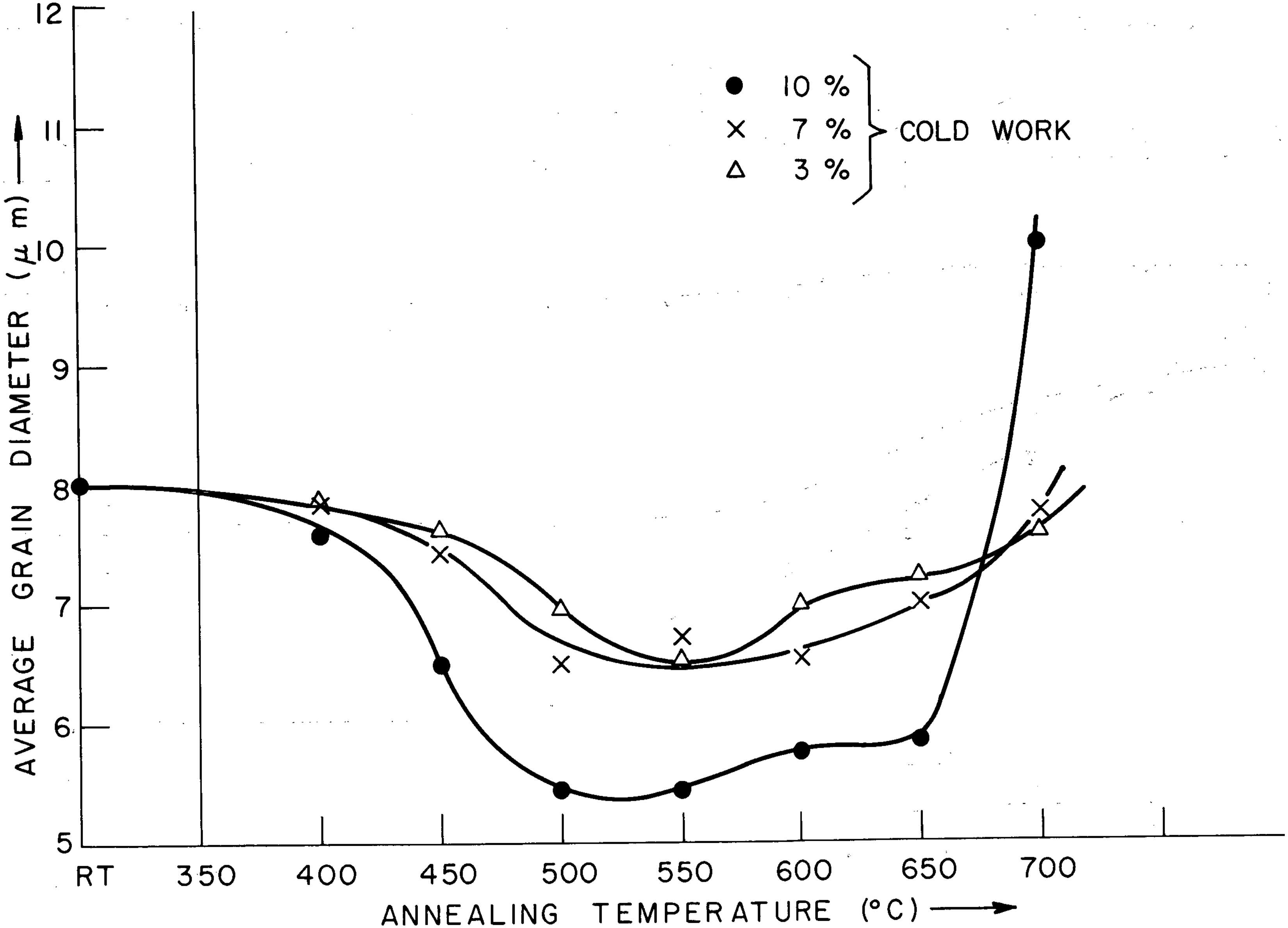


Figure 15

Change in average grain size with annealing temperature. Sample 313 (3.27 wt% Si, 600 ppm C).

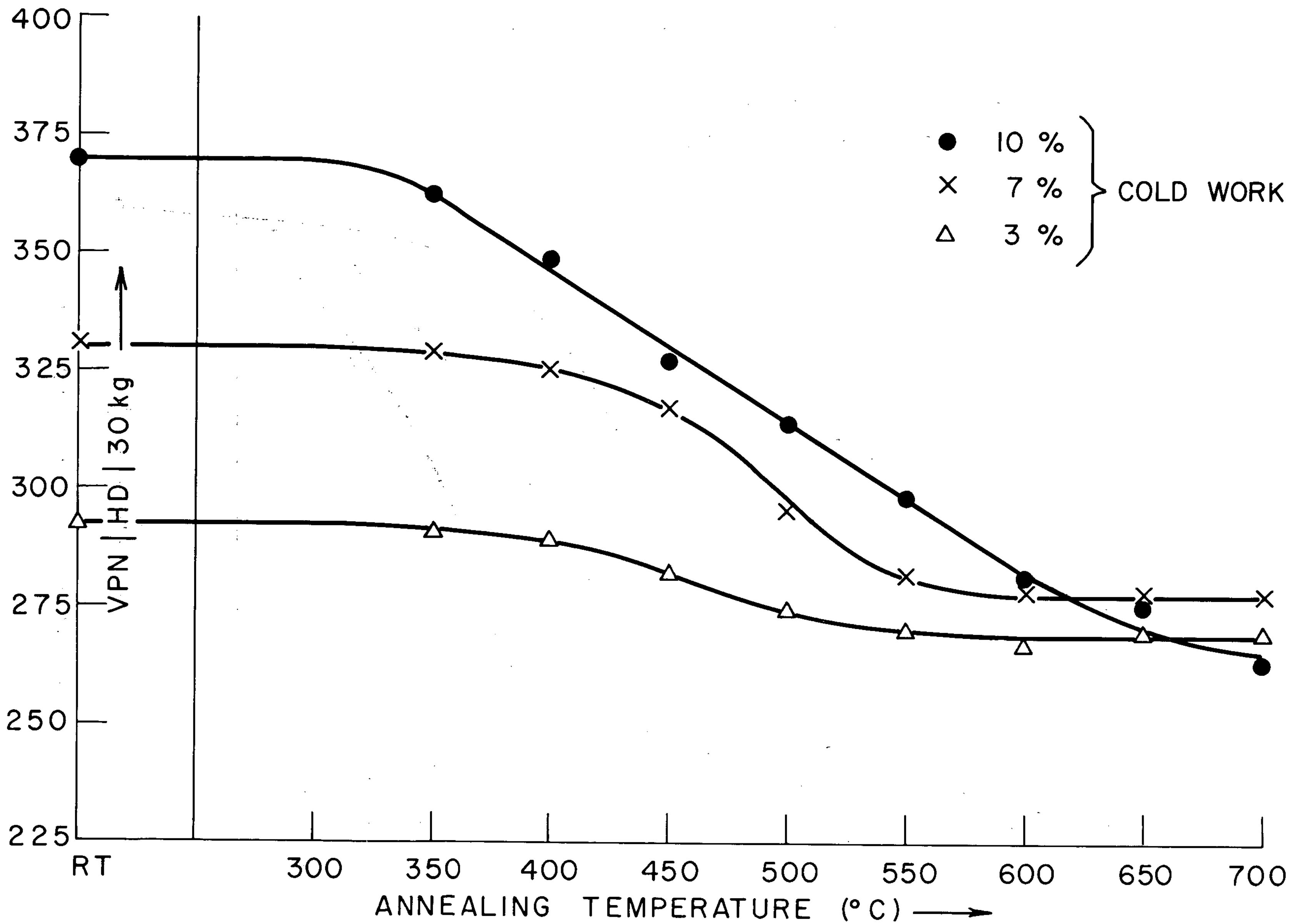


Figure 16
Change in hardness with annealing temperature. Sample 300 (4.02 wt% Si, 140 ppm C).

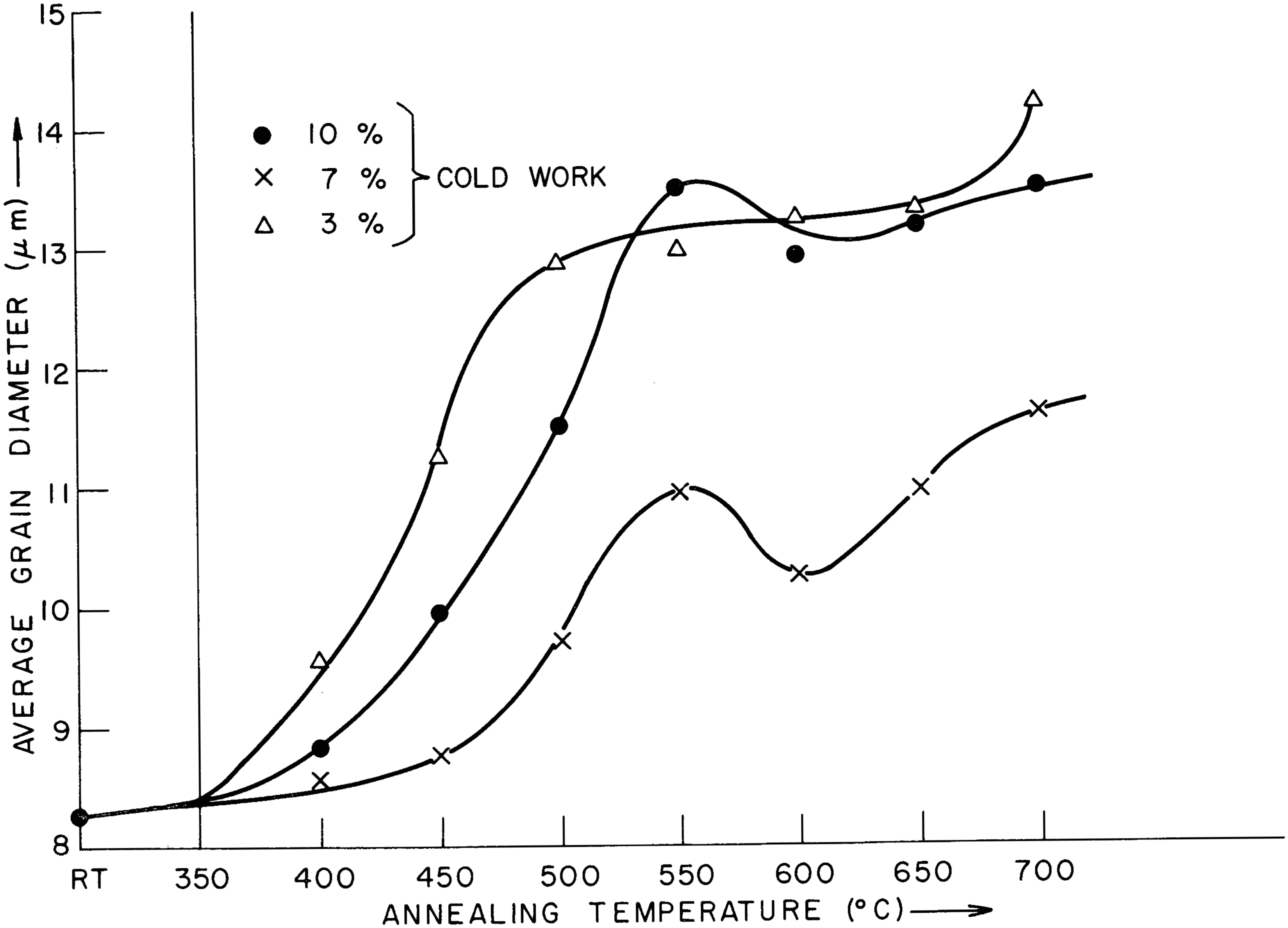


Figure 17

Change in average grain size with annealing temperature. Sample 300 (4.02 wt% Si, 140 ppm C).

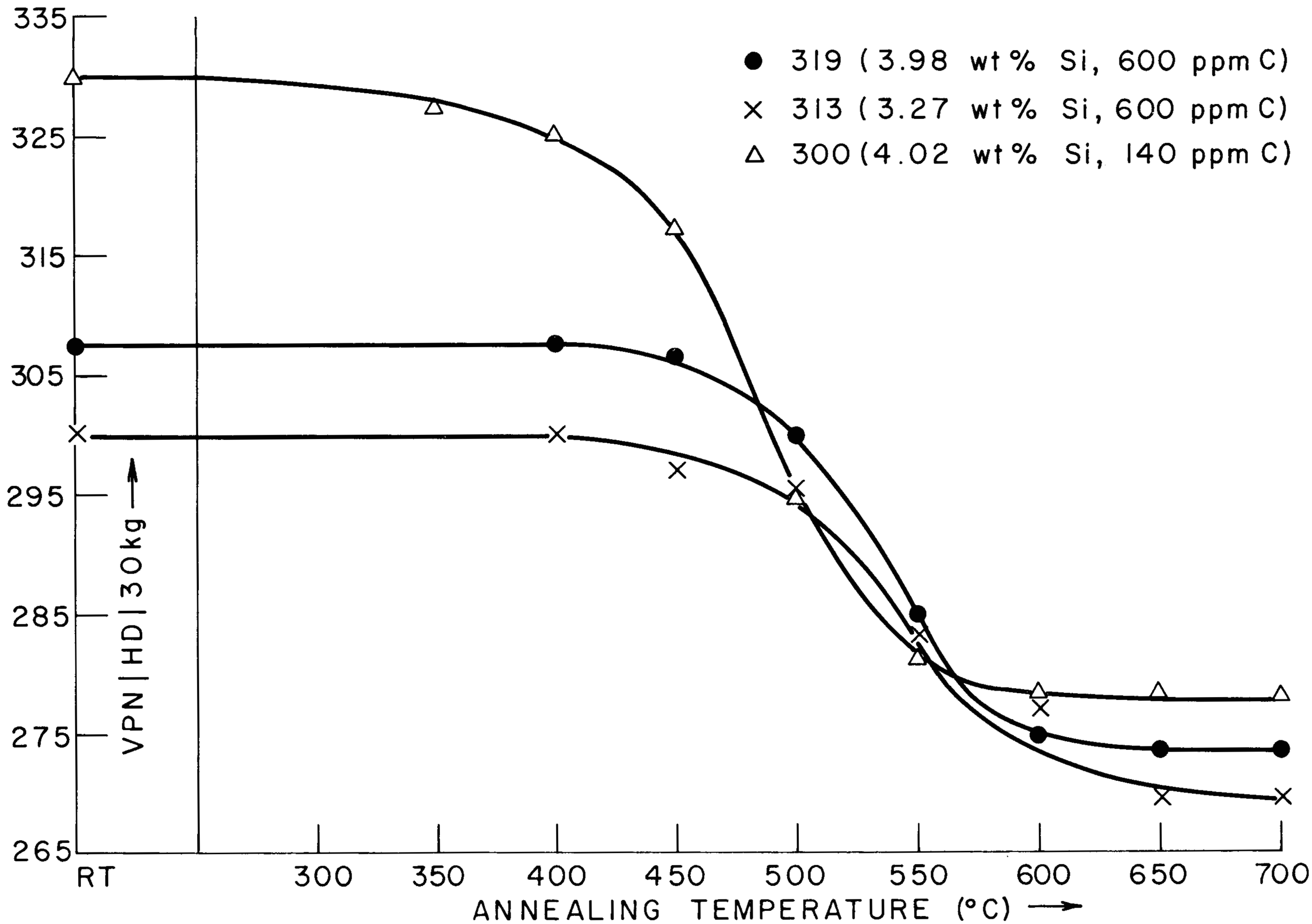


Figure 18

Change in hardness with annealing temperature for three samples cold worked 7%.

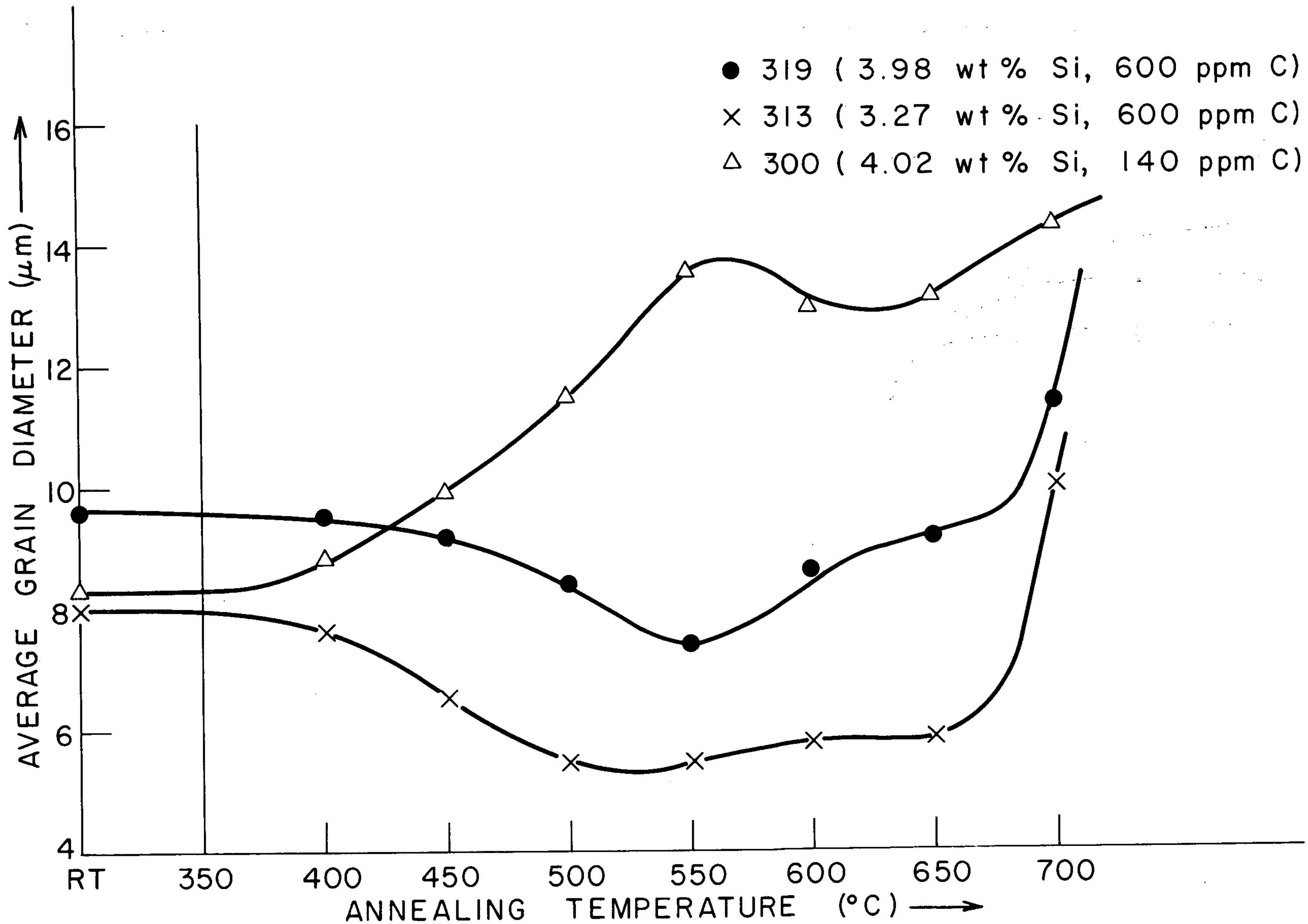


Figure 19

Change in average grain size with annealing temperature for three samples cold worked 10%.