Title
METALLURGY LECTURE SERIES - LECTURE I

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Author
Nickerson, R. A.

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UNIVERSITY OF CALIFORNIA
Radiation Laboratory
Berkeley, California

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METALLURGY LECTURE SERIES

Lecture I
May 7, 1952
R. A. Nickerson

INTRODUCTION

This is the first of a series of discussions of subjects in physical metallurgy of interest to the Radiation Laboratory. Sheets circularized lately for the purpose of indicating interest in such discussion showed such a range and breadth of subject matter that selection of only a few related ones seems practical for each session.

This session will be devoted to the background for, and some of the factors involved in, the heat treatment of steel and the precipitation hardening of Berrylium Copper. The second and third lectures will be devoted to joining problems and the magnetic properties of metals.

HEAT TREATMENT

In addition to the property of chemical union to form the normal polar compounds or salts such as Ferric Chloride or Copper Nitrate metals possess the property of interfusion or alloying. This alloying tendency may vary from simple mechanical mixtures of the components to the truly involved intermetallic phases such as Fe_3C, $Cu\ Al_2$ or Be Cu with many of the properties of the polar compounds. By reason of the varied structures possible and the way they may be altered by heating and cooling, the original properties of the parent metals of the alloy become modified and often new and unexpected ones are created. It is on the basis of this internal structure of the solid alloy that physical metallurgy explains properties. In turn, the basis for the systematic study of an alloy is its constitution diagram which represents equilibrium in the alloy system at a given temperature. Only the systems of two elements or binary alloys can be simply described, so I shall confine this discussion to them.

The simplest form of this diagram shows, for any composition of alloy, the temperature at which particular phases are in equilibrium, as well as the composition of those phases.

The number of binary or two metal component alloy diagrams is large and specific relationships are peculiar to each pair of alloying elements. Happily, however, all of the commonly encountered diagrams possess certain portions which permit classification into just five main features or reactions. The whole diagram of alloy equilibrium, then, may be thought of as composed of combinations of these five simple features. The Cu-Zn diagram of the brasses, for instance, contains six while Al-Si alloys of which Alcoa casting alloy 43 is an example, is completely described by just one of these simple diagrams.

Let us go over, just briefly, these five features, then apply them to the Fe-C system and the Cu-Be system as an aid in explaining their heat treatment.

The first is that in which there is no solubility in either the liquid or the solid state. These alloys, or better, mechanical mixtures, separate on melting, into layers and, even if stirred, solidify with no solution. The lead in the free machining brasses and bronzes is one example of this type. The lead occurs in the final alloy as small globules of pure lead, soft, and unalloyed. Care must be taken in the melting and casting to insure mixing of all the lead and in solidification to insure its being segregated uniformly throughout the casting. The 85% Copper, 5 Tin, 5 Zinc, 5 Lead alloy used as a bronze casting material here at this Laboratory is subject to lead segregation. Other examples of this group are W-Ag, W-Cu, Mo-Cu, and Mo-Ag. These materials must be formed into their final shape by mixing, pressing, and sintering their metal powders; the result is a group of electrical contact materials with properties unattainable by any other method of manufacture.

The second type of diagram (Fig. 1) is of interest mainly for its casting qualities. The components are only partially soluble in both solid and liquid states. The system Cu-S is of this type and the 2 melt area is of consequence in the refining of Copper Sulphide ores. Cu-Cr is also of this type and causes difficulties in the making of Cu-Cr master alloys for the making of Westinghouse's Cupaloy which is used here in the Laboratory.

The occurance of the next three types is more common in the industrially important alloys.

The third is the Peritectic or liquid A_s B_s (Fig. 2) which occurs in the solidification process when the liquid and that portion of the alloy which as already solidified react to form a new phase; or the new phase upon reaction may be an intermetallic compound, (Fig. 3) which is a phase formed between the two metals in a certain combining ratio, as a salt, such as 1 : 1 in Be Cu or 3 : 1 in Fe_3C; or as Fe_3P which is called Steadite and occurs in cast irons, or the compounds of Cr_4C; Cr_7C_3; or in the compound of Silver and Mercury in its amalgamation process. These reactions produce a structure (Fig. 4) which stops itself by the formation of a wall of reaction products and requires long high temperature "soaking" to become homogeneous or "even" in composition throughout.

The fourth phase diagram component is the eutectic, in which liquid A_s B_s. (Fig. 5) This reaction, that of liquid solidifying at a single temperature lower than the solidification/temperature of either of the components from which it is formed, has many practical consequences. To point out a familiar one, that of the Handy Harman Cu-Ag "BT" alloy for silver soldering (Fig. 6) which melts some 330°F below the melting point of Copper, due to the formation of a eutectic. The structure of these eutectics is varied (Fig. 7) as in the Cu-Cu_2O system, (Fig. 8) or the Al-Si casting alloy of Alcoa, (Fig. 9) or this Cu-Cu_3 Peutectic which occurs in Handy Harman Sil-Fos solder, or others such as (Fig. 10) Cd-Zn or (Fig. 11) Cd-Sn.

The fifth type of alloy system (Fig. 12) represents complete solubility in both liquid and solid states. At this point the difference between the ideal equilibrium conditions and those actually encountered are best introduced. Consider the alloy x - x' solidifying. The first solid to nucleate is of composition "f".

The liquid changes in composition from "a" to "g", the solid from "f" to "C" or some line below F-C. This leads to demdritic segregation or coring of the grains as (Fig. 13) in this Cu-Ni alloy. This is the usual structure of cast alloys and often requires long homogenizing treatments to attain the composition actually desired.

THE IRON CARBON DIAGRAM

A look, now, at the Iron Carbon diagram (Fig. 14) shows two of the last three diagram types. A Peritectic, and a eutectic. The region of most interest is the eutectoid section (merely a eutectic in which all reactants are solids). The appearance of structures resulting from slow cooling of several Iron Carbon alloys is similar to those seen above for the various partial diagrams. (Fig. 15, 16, 17, and 18)

THE TRANSFORMATIONS IN STEEL

Any introduction to heat treatment of steel must begin with the work of E. C. Bain, of U. S. Steel Laboratories in 1930. This work formed the basis for removing heat-treatment of steel from the art of the village blacksmith to the scientific industrial tool that it is today. (Fig. 19) Since all the hardening of steel comes about by the transformation of austenite at temperatures below its stability temperature, Bain's investigation concerned itself with the products of that transformation as a function of time as the temperature was lowered.

He used small rod specimens for rapid heat transfer and, after austenitizing, or converting to austenite, the high temperature, non-magnetic form of iron in which carbon is completely dissolved, at 1340°F, he rapidly quenched them in lead baths at constant temperatures below 1340°F. After holding for a given length of time at this isolthermal transformation temperature, the sample was then quenched in cold water. The microstructure then showed how far the transformation had proceeded at that temperature and time. The products he observed were:

1. Pearlite, the equilibrium transformation product of the eutectoid reaction, of increasing fineness to the critical temperature.

2. Martensite, the supersaturated solution of carbon of high hardness and tensile strength.

3. Bainite, Ferrite and Fe_3C, which resulted from a reaction other than the eutectoid.

Later work of Grenenger and Troiano corrected some of the errors in the lower section of Bain's curves and showed them to as shown in (Fig. 20). The error of Bain's conclusions was that the M_s temperature varied with time. Actually, what he observed was a mixture of tempering of the martensite formed and his inability to prevent further transformation as he cooled the quenched samples to room temperature.

The "S" curve of Bain or Troiano's "C" curve has been improved upon, from a practical standpoint, in a later modification of this curve (Fig. 21) which correlates dynamic cooling rates with the transformation-time-temperature diagram. This type of diagram, coupled with the Jominy end-quench test for hardenability, gives all of the factors of steel treatment necessary for prediction of hardness, depth of penetration of hardening, structure produced, and cooling rate studies of complex section.

The hardness produced in quenching of steels is primarily dependent upon the carbon content (Fig. 22). The main purpose of alloying elements in steel is to permit lower cooling rates, with their attendant lowering of warpage, distortion, and thermal stressing. The effect is to move the C curve to the right.

Steels are seldom used in the fully hardened condition (Fig. 23) for they are brittle and lack the impact toughness to resist shock. Therefore they are subjected to a further heating cycle known as tempering. Since martensite is a non-equilibrium, or better, a "metastable", structure, further heating permits the controlled return to equilibrium, which, from the phase diagram, is seen to be Ferrite and Fe_3C. As the tempering temperature increases, the return to equilibrium is more rapid and more complete; but for a given time and temperature of tempering, the process goes only so far. Thus for each hardened steel there is a certain tempering temperature which will give a certain set of properties, hardness, tensile strength, impact toughness, and internal structure. The steps in this process are:

1. $\alpha - \beta$ martensite, lattice changes.
2. Rejection of Fe_3C in a series of structures which have been given the names of Sorbite, Troostite, and Spheroidite.

The end product of a fully spherodized steel being Ferrite and iron carbide entirely equivalent to the slowly cooled steel products, but entirely due to fine structure differences, tougher and more suitable to cold forming, for the Fe_3C is in the form of small spheres and the Ferrite the continuous background phase.

HEAT TREATMENT FOR RECRYSTALLIZATION

Many of the commercially important alloys are not heat-treatable in the way that steel is. That is, their hardness is not alterable by the transformation mechanism. In this class of materials are the pure metals, Al and 2SAl alloy, Copper, brass, phosphor-bronze spring stock, the 300 series stainless steels, armco ingot iron, Monel, to name but a few. The only way in which their properties can be altered is by cold-deformation and annealing to control their state of work hardening and their grain size.

Copper sheet, when cold rolled, becomes harder. (Fig. 24) Its hardness, tensile strength, and grain size are determined by the severity of the last cold reduction after a process anneal and its final heat treatment.

With the changes in hardness upon reheating there is first a stress relief, then growth of new grains within the metal from nucleation points of high stress. (Fig. 25) The size of the regrown grains depends upon how many nucleii there are formed and the growth rate of these nucleii. In other words, time of anneal, temperature of anneal, and how much cold work has been performed, all determine the final properties. (Fig. 26) This shows a typical study of recrystallization and the dependence of the factors named before. Here is a specific study of Aluminum showing the <u>rate</u> of heating dependence, (Fig. 27 and 28). Or schematically in (Fig. 29), the usual method of showing this data for an alloy, here brass of the 70 - 30 or cartridge brass composition, (Fig. 30).

A graphic demonstration of this variation is shown in (Fig. 31) where the amount of working varies with distance from a bullet hole in a tin sheet, and results in a wide range of cold work, note that the grain size is largest for percentage of cold work which is rather small.

PRECIPITATION HARDENING OF BERYLLIUM COPPER

Beryllium Copper is one example of a group of alloys which are hardenable by heat treatment. The mechanism of hardening, however, is completely different from that which hardens steel. The hardenable aluminum alloys, copper-bearing steels, K-Monel, and another new one recently introduced by Eitel-McCollough of San Bruno, a Beryllium Copper substitute composed of Copper, Manganese and Nickel, are other examples.

To show a gain of mechanical strength and hardness with time at some low age hardening temperature, an alloy must exhibit (Fig. 32) a decrease in solubility with decrease in temperature. At some high temperatures the alloy must consist of a single solid solution, or hold appreciably more of some alloying element in solution than it does at room temperature. Also, it must be able to retain that solution at room temperature when quenched or cooled rapidly from the high, or solution treating temperature. When quenched it is a supersaturated solution which, when heated, tries to attain the equilibrium solubility by precipitating its excess solute. Usually this precipitating phase is a compound ; in Beryllium Copper it is Cu-Be; in 24ST Aluminum alloy it is $CuAl_2$, and Mg_2Si in 61ST.

From the Cu-Be phase diagram (Fig. 33) the decrease in solubility for Beryllium is seen to be from about 2% at the solution heat treating temperature, 1400°F, to less than 0.2% at room temperature. The fact that the "A" temper of soft, solution treated strip does not harden with time indicates that it does not "naturally" age, or spontaneously precipitate Be-Cu at room temperature, as do some of the aluminum alloys which, indeed, must be held below room temperature in cold boxes to prevent this "natural" aging.

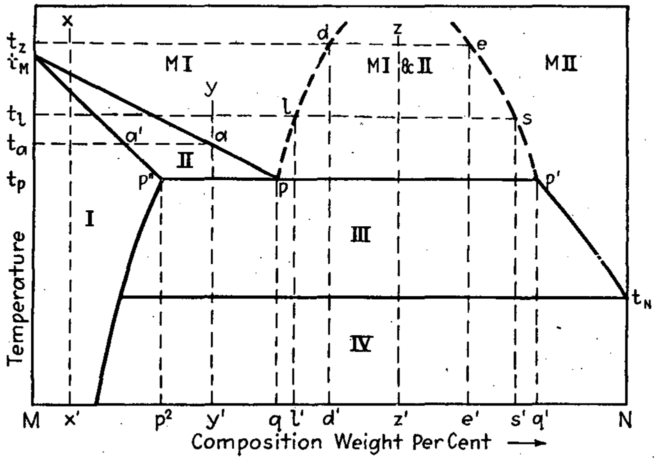
If held for too long a period at too high an aging temperature, i.e. 600°F, all of the Cu-Be that is supersaturated will come out of solution (Fig. 34) and again the material will be soft and ductile, as it will when properly solution heat treated and quenched.

Thus the hardening effect will be seen to occur intermediately between full solution and full precipitation. Beryllium is distributed at random throughout the copper in the solution heat treated state at an atomic concentration of about 1 in 5 atoms.

As a precipitate it is concentrated to Be-Cu compound at 1 to 1 atomic concentration. As it is concentrating to form the precipitate, the greatest hardening occurs throughout all the solution. When the precipitate is fully formed the strains in the then Beryllium-free copper grains are relieved and the hardness again beings to drop. This is <u>overaging</u>.

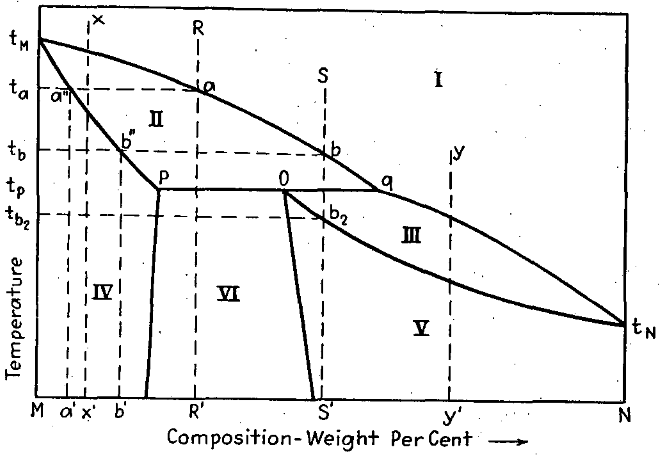
The condition of strain in the material prior to aging also has an influence on the properties attainable after aging, for cold work provides slip planes and distortions of the grain material which permit more uniform nucleation of the precipitate (Fig. 35). Here we see the effect of proper aging and over-aging on strip which was in the annealed, 1/4 H, 1/2 H and hard states. The original tensile strength of from 73 - 95,000 psi yield aged strengths of from 160 to 185,000 psi.

RAN:plc



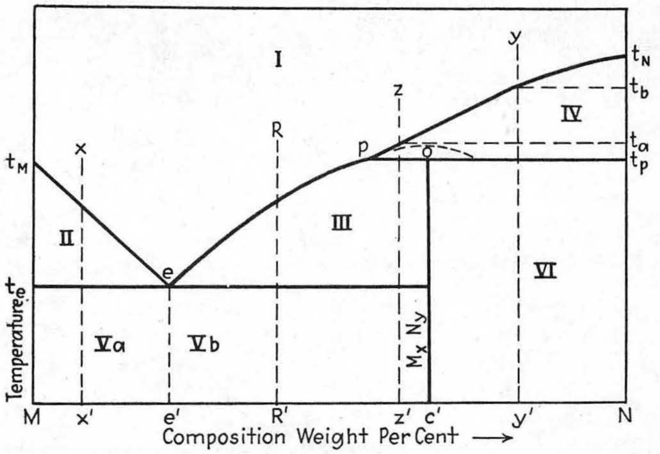
Equilibrium diagram of metals *M* and *N*, which are partially soluble in each other in both the liquid and solid states.

Fig. 1



Equilibrium diagram of metals *M* and *N*, which are completely soluble in the liquid state, and partially so in the solid state. A peritectic reaction, on cooling, results in the formation of a solid solution.

Fig. 2



Equilibrium diagram of metals *M* and *N*, which are completely soluble in the liquid state and incompletely soluble in the solid state. A peritectic reaction, on cooling, results in the formation of a compound *MN*.

Fig. 3

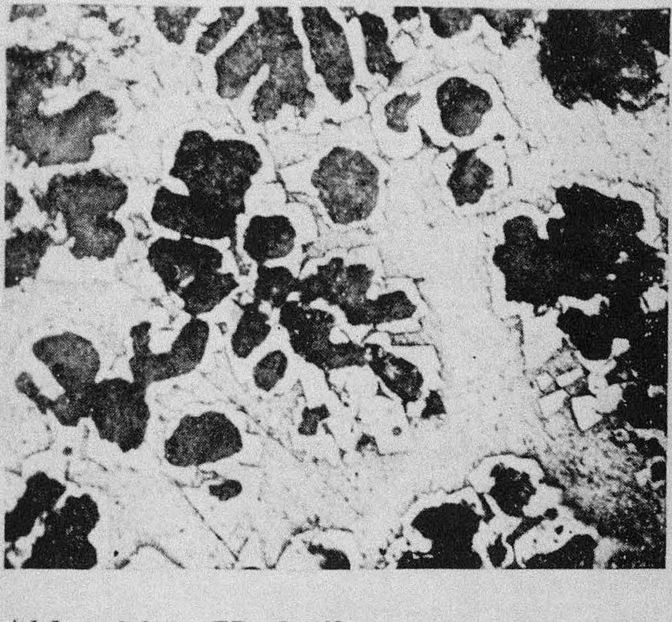
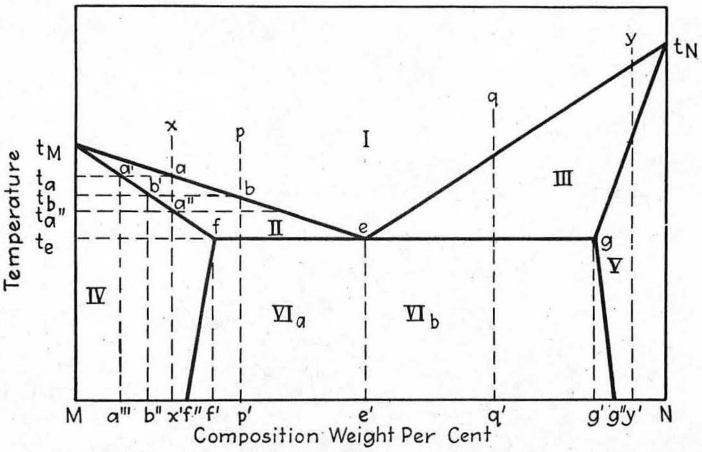


Abb. 176a. Umhüllung einer Kristallart durch eine andere.

ZN266

Fig. 4



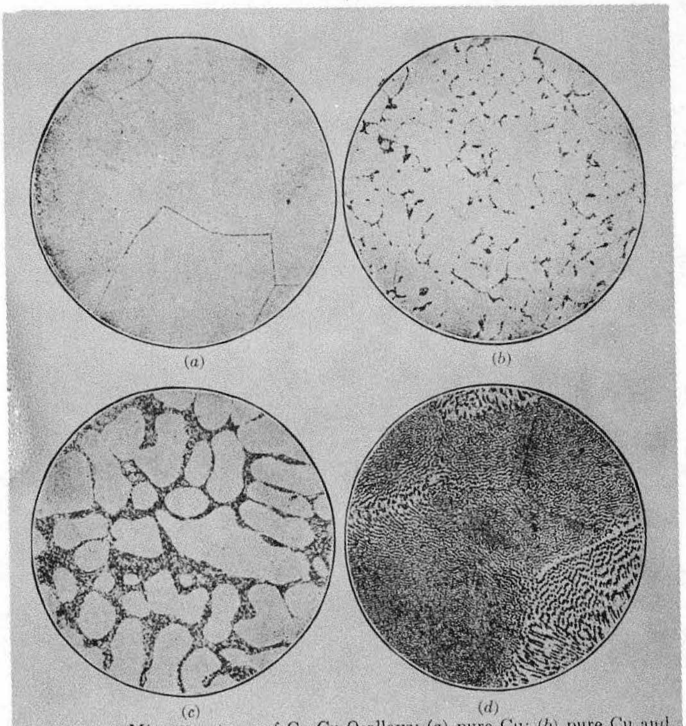
Equilibrium diagram of metals *M* and *N*, which exhibit unlimited liquid solubility, and partial solid solubility.

Fig. 5

Copper-silver alloy (cast). 100 ×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

ZN264

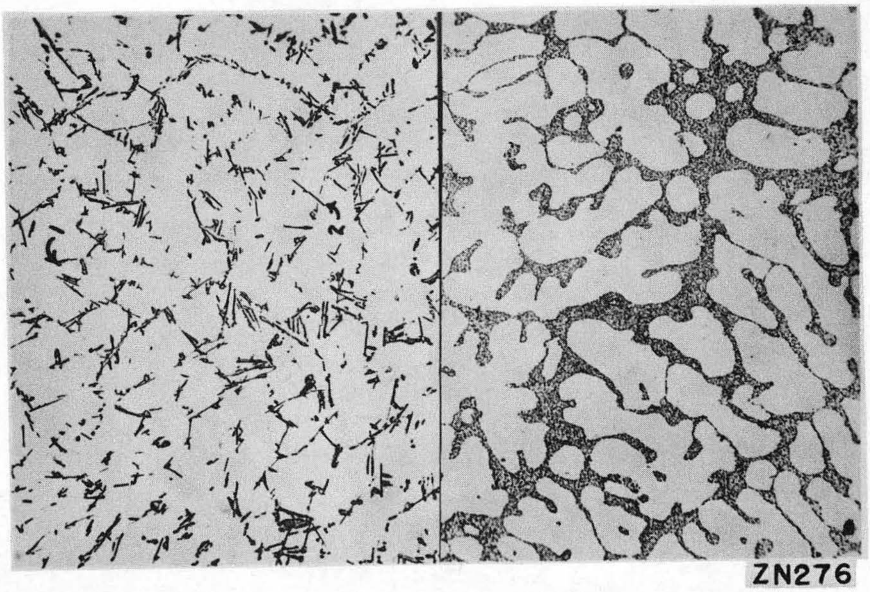
Fig. 6



Microstructures of Cu-Cu_2O alloys: (a) pure Cu; (b) pure Cu and eutectic; (c) Cu + eutectic (higher Cu_2O content); (d) pure eutectic at 3.3 per cent Cu_2O. (*Courtesy of Homerberg and Williams.*)

ZN262

Fig. 7



ZN276

Fig. 8

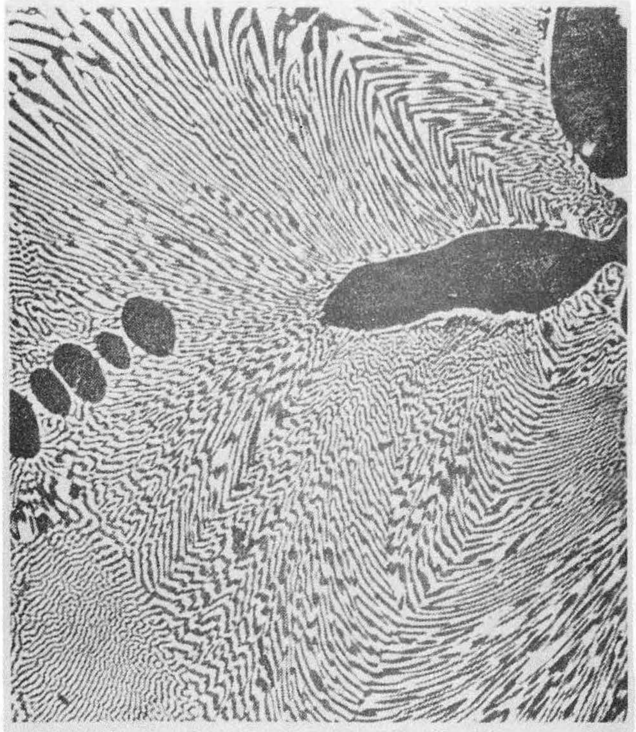


FIG. 135. Cu-Cu_3P eutectic. ×250.

ZN272

Fig. 9

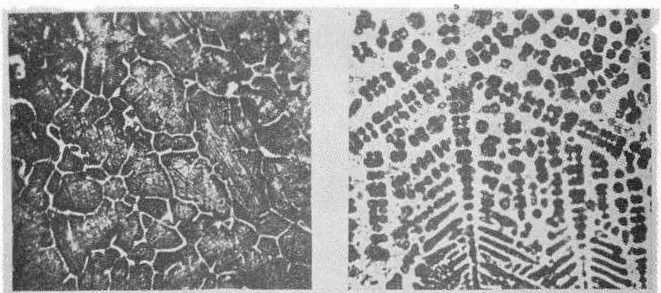


Abb. 161. Gefüge einer Legierung mit 95% Zn und 5% Cd: Zink (dunkel) primär ausgeschieden.

Abb. 162. Gefüge einer Legierung mit 50% Zn und 50% Cd: Zink (dunkel) primär ausgeschieden.

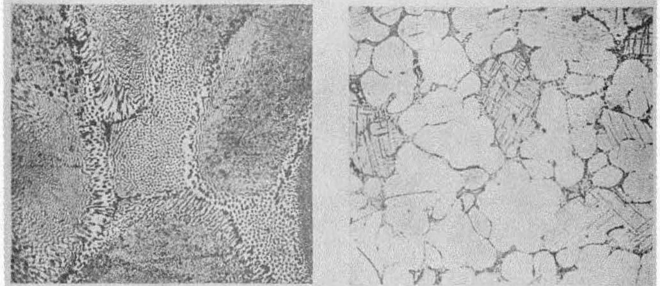


Abb. 163. Gefüge einer Legierung mit 18% Zn und 82% Cd: Eutektikum aus Zink und Cadmium.

Abb. 164. Gefüge einer Legierung mit 10% Zn und 90% Cd: Cadmium (hell) primär ausgeschieden.

ZN268

Fig. 10

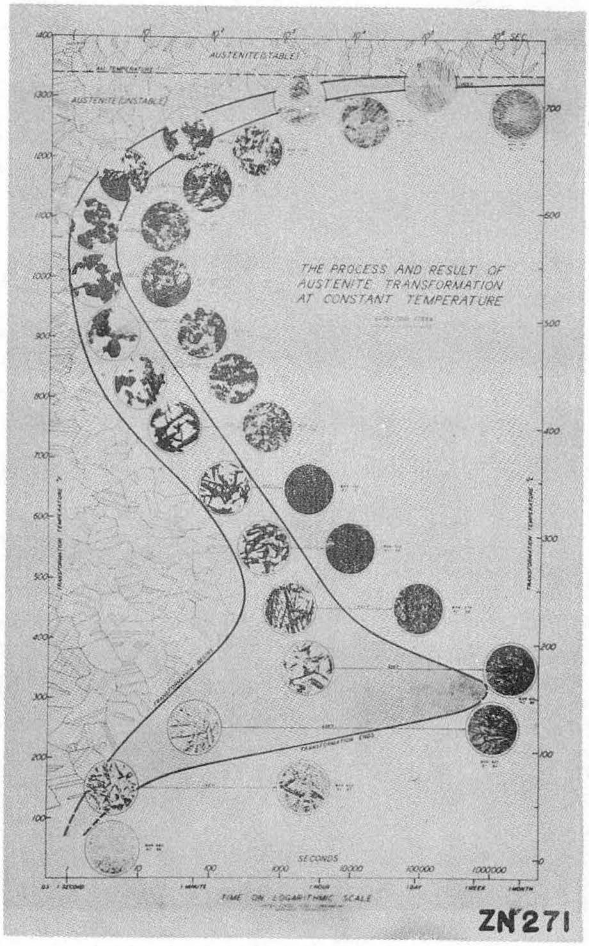
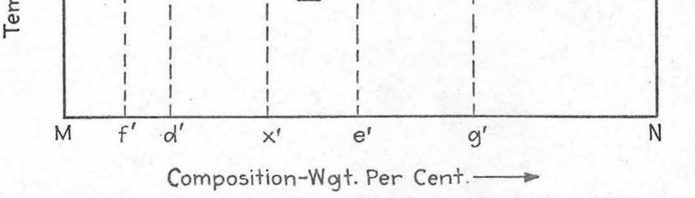


Fig. 11



Equilibrium diagram of metals *M* and *N*, which exhibit unlimited solubility in each other in both the liquid and solid states.

Fig. 12

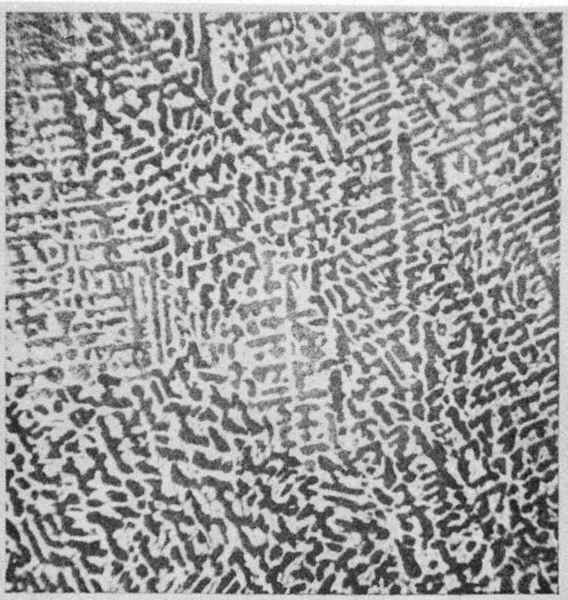
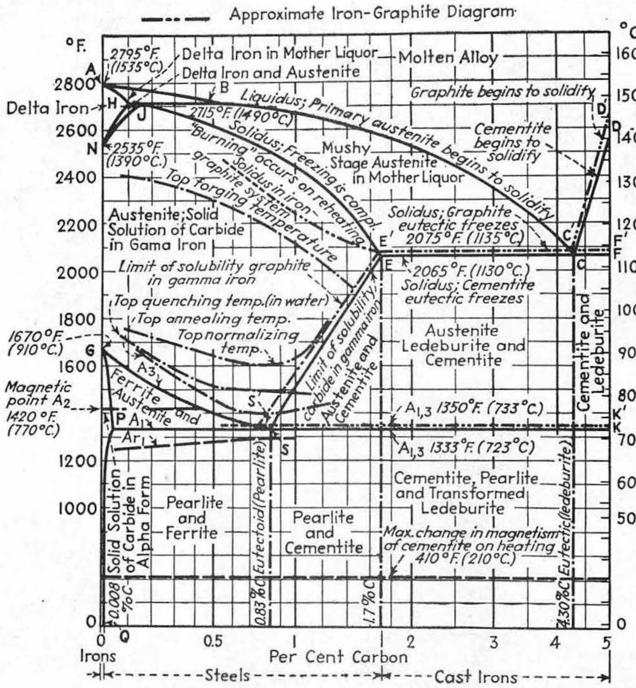


Fig. 104. Cu-Ni alloy: 50 per cent. Cu, 50 per cent. Ni. As cast. × 100.

ZN274

Fig. 13



The iron-carbon diagram. (*Metals Progress*, 1940 *Reference Issue*.)

Fig. 14

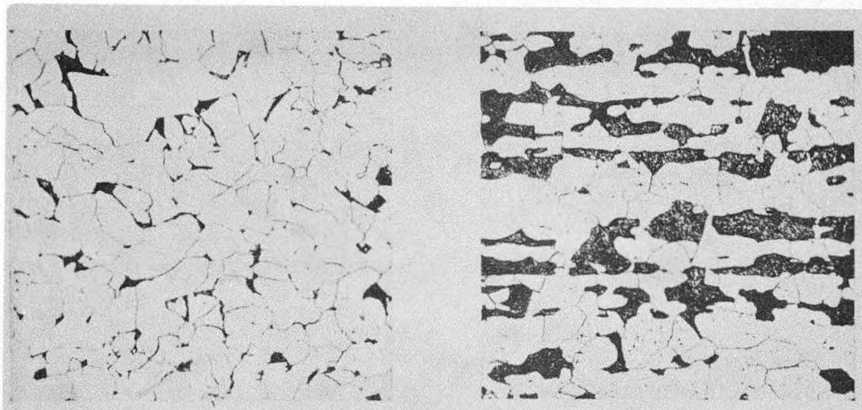


Fig. 277. Slowly cooled steel 0·1 per cent. C. × 100.

Fig. 278. Slowly cooled steel 0·28 per cent. C. × 100.

ZN265

Fig. 15

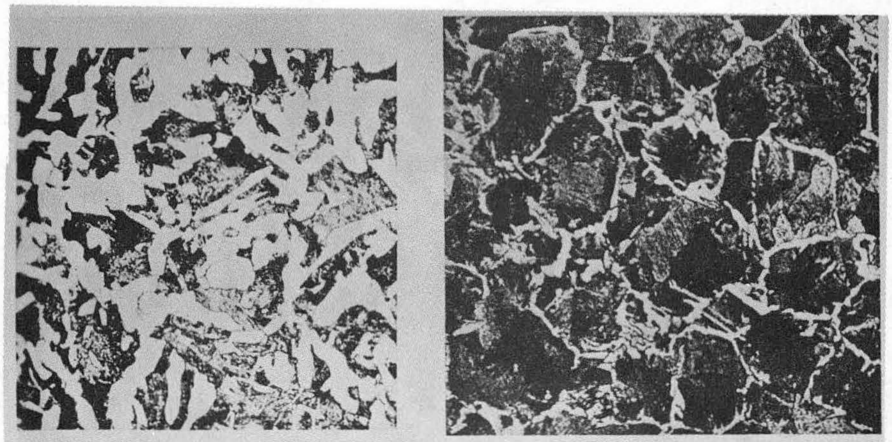


Fig. 279. Slowly cooled steel 0·43 per cent. C. × 100.

Fig. 280. Slowly cooled steel 0·73 per cent. C. × 100.

ZN273

Fig. 16

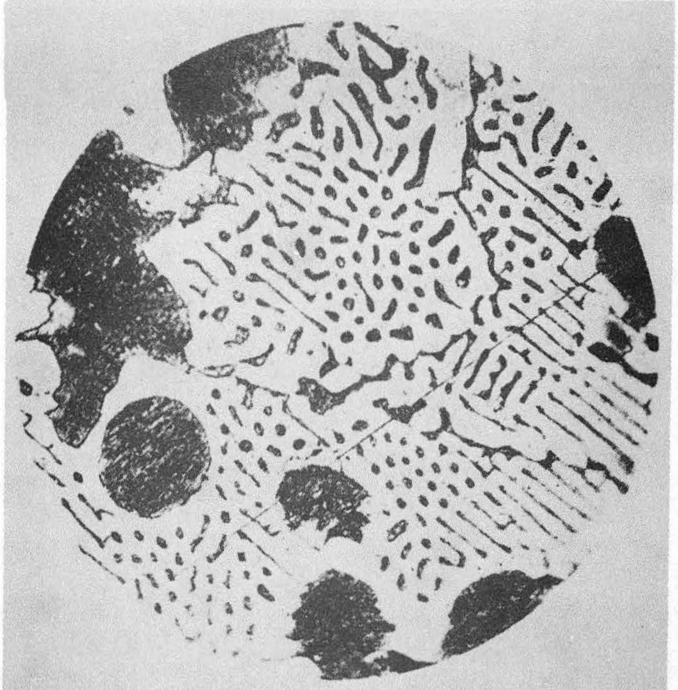


Fig. 139. Eutectic structure in iron-carbon alloys. ×820.

ZN270

Fig. 17

Fig. 493. Flake graphite, pearlite, and ferrite. ×400.

ZN267

Fig. 18

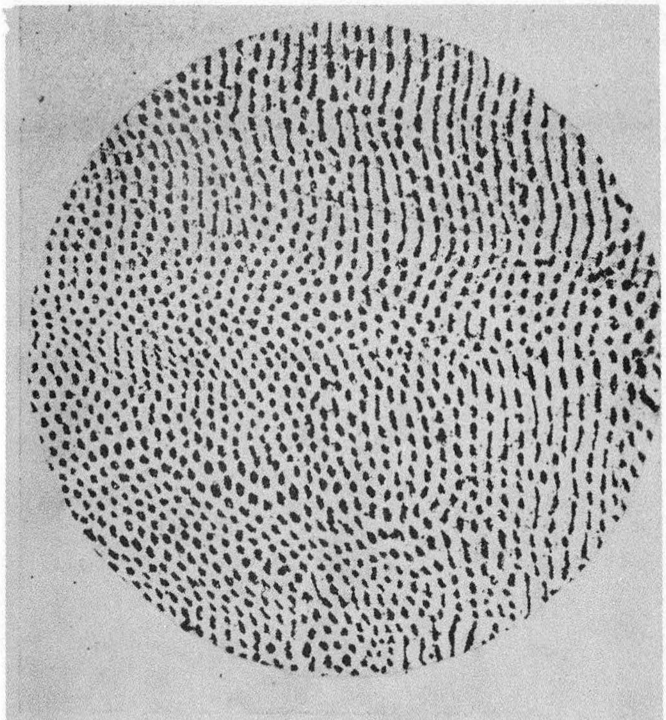
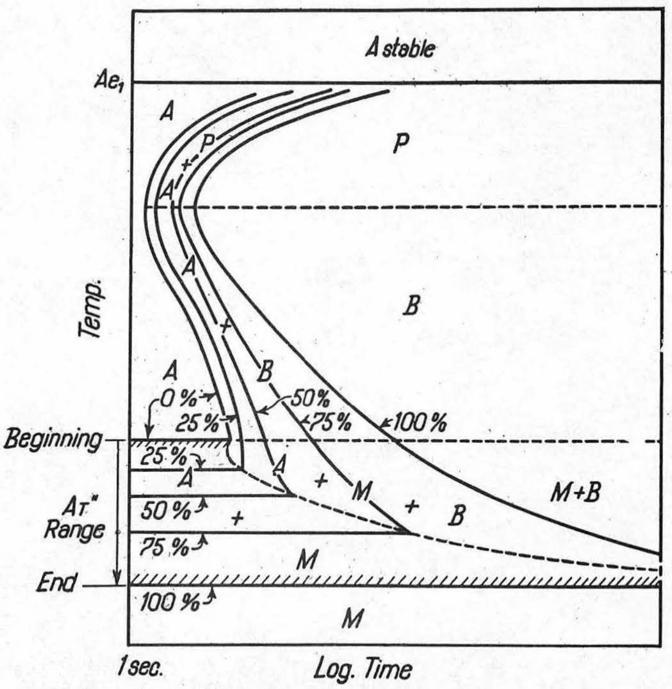


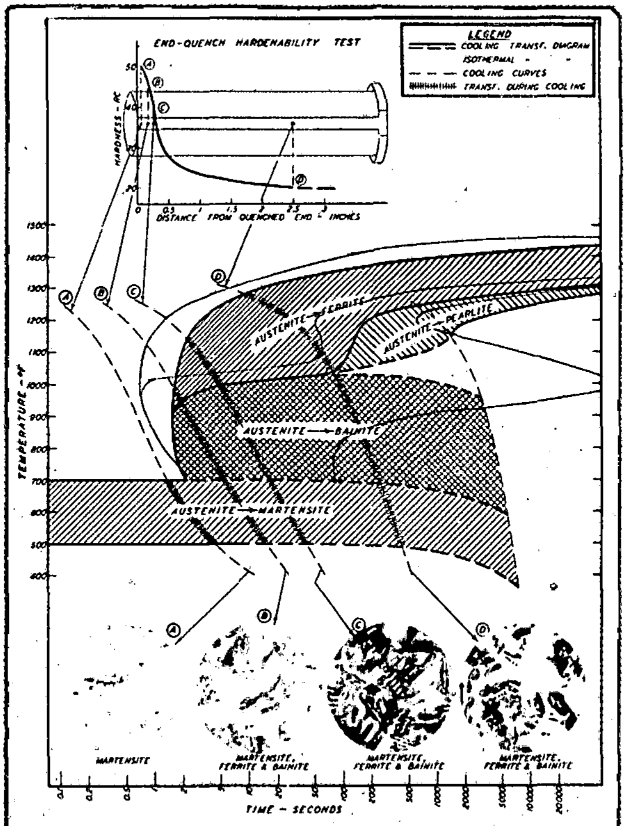
FIG. 138. Cadmium tin eutectic. ×165. (*Journal of the Institute of Metals.*) ZN275

Fig. 19



A—Modified S-Curve Diagram. Full Lines Represent Per Cent of Austenite Transformed. A = Austenite, P = Pearlite, B = Bainite, M = **Martensite** or Tempered Martensite.

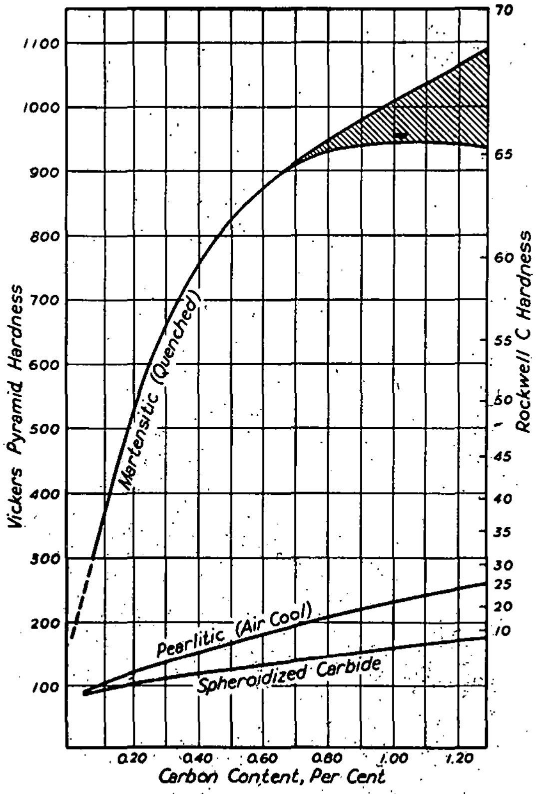
Fig. 20



Correlation of continuous cooling and Isothermal Transformation Diagrams with End-Quench Hardenability Test Data for an 8630 type steel.

ZN261

Fig. 21



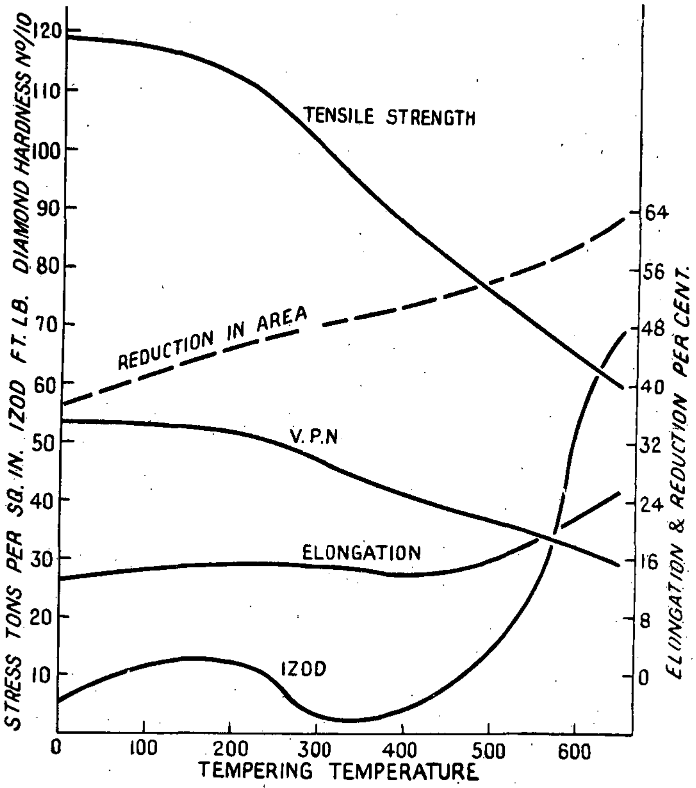
The Hardness of Carbon Steels in Three Structural Conditions as a Function of Carbon Content: (Approximate).

Top Curve—Fully-Hardened Martensite.

Middle Curve—Lamellar Structure (with Proeutectoid Constituents) as Formed in Normal Cooling after Rolling.

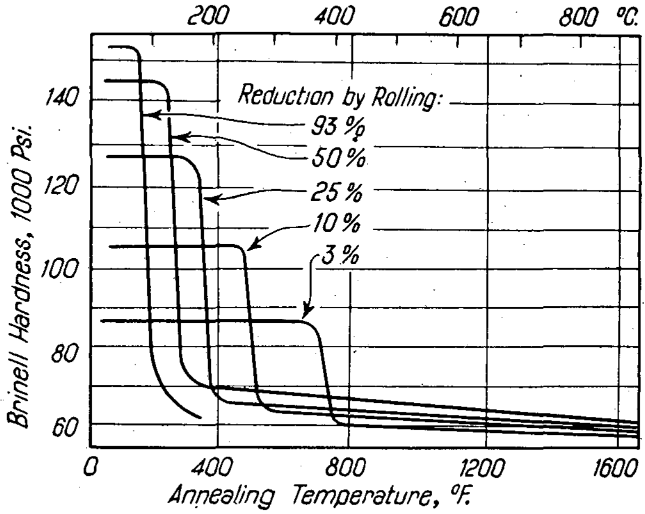
Bottom Curve—Carbide Coarsely Spheroidized. Minimum Hardness Commercially Obtainable.

Fig. 22



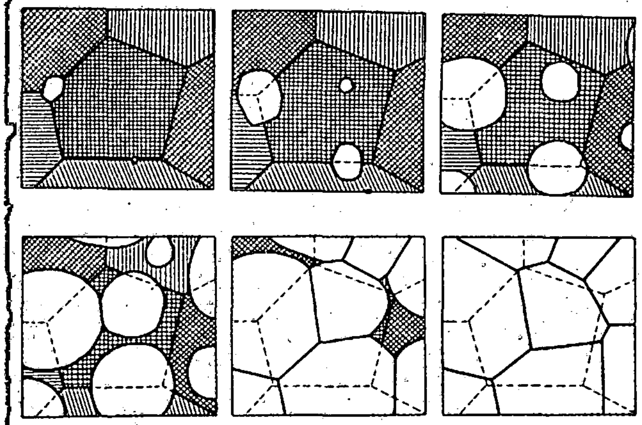
Properties of hardened and **tempered** Ni-Cr steel.

Fig. 23



The decrease in hardness produced by the annealing of copper sheet that previously received different reductions by rolling. (Koester)

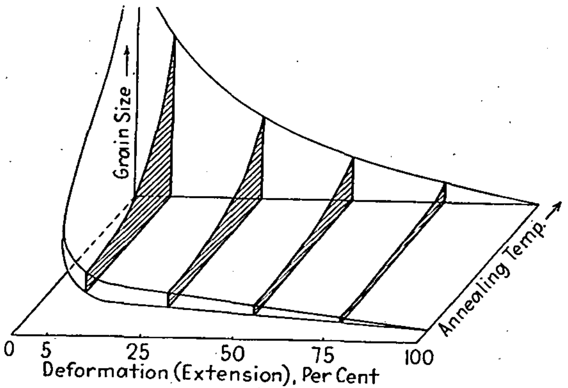
Fig. 24



Schematic illustration of crystal growth in a recrystallizing metal. (*R. F. Mehl.*)

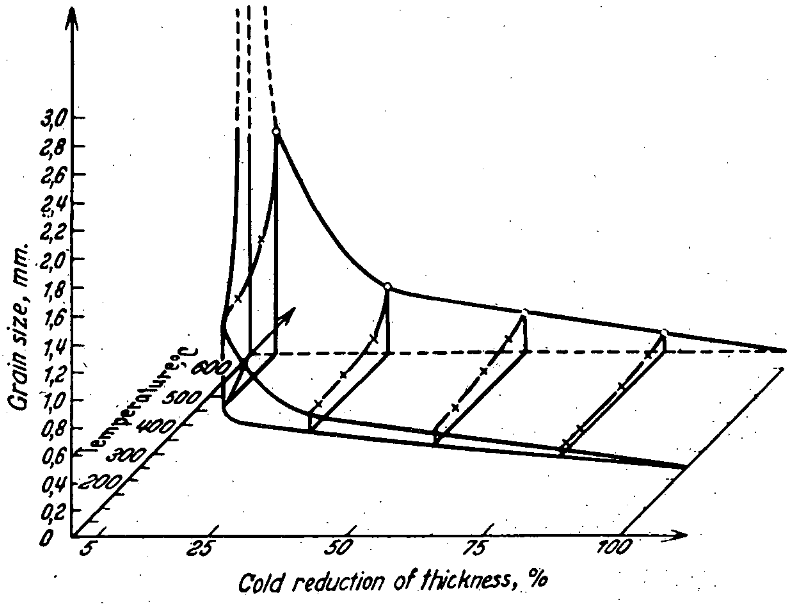
ZN260

Fig. 25



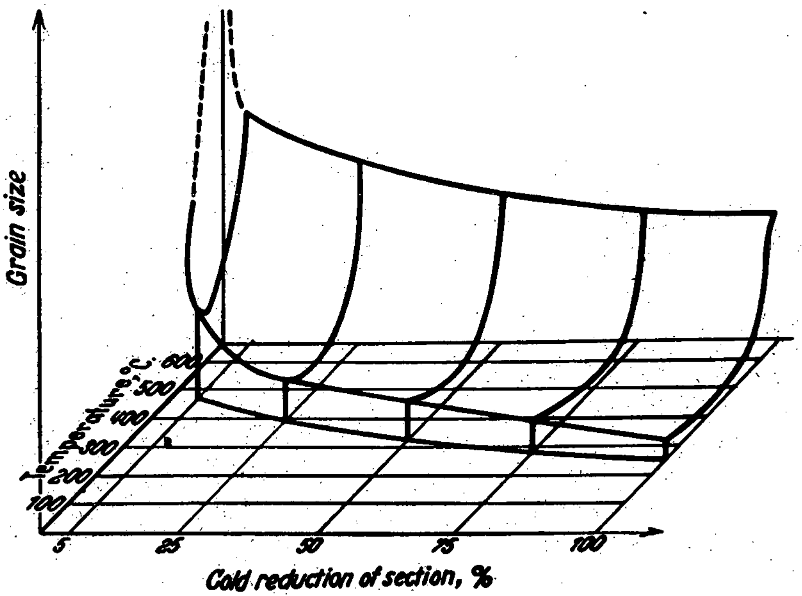
Recrystallization (grain-growth) diagram of a metal. (*After Czochralski.*)

Fig. 26



–Recrystallization diagram for aluminum (Loofs-Rassow and Velde).

Fig. 27



—Recrystallization diagram for aluminum; rapid heating.

Fig. 28

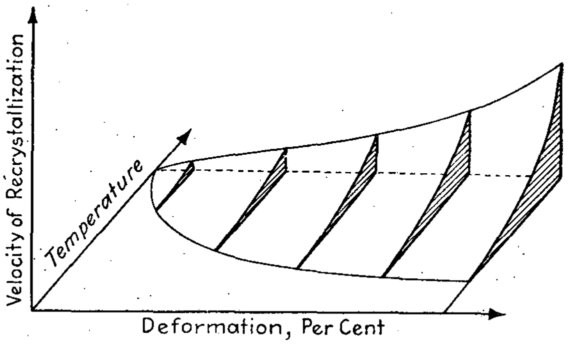


Diagram illustrating the relation between the velocity of recrystallization, the temperature, and the amount of previous deformation. (*After Czochralski.*)

Fig. 29

CHARACTERISTIC ANNEALING CURVES 70-30 BRASS

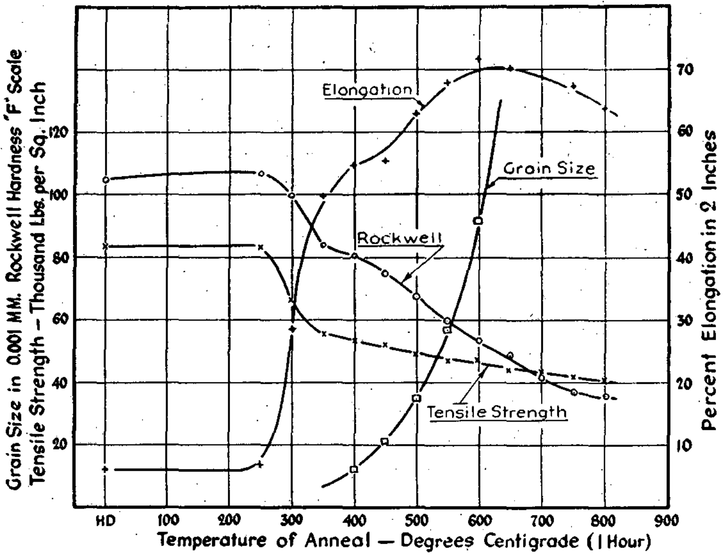


Fig. 30

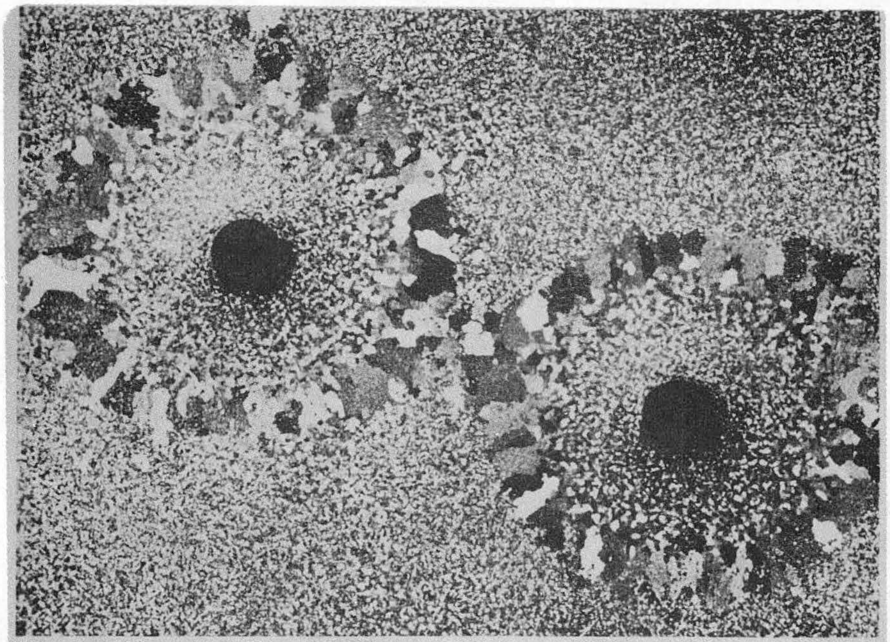
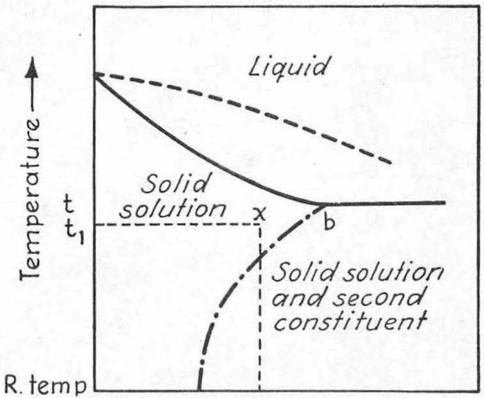


Abb. 170. Durchschossenes, geglühtes Sn-Blech (415). **ZN269**

Fig. 31



Temperature-solubility relationships in an age-hardening system.

Fig. 32

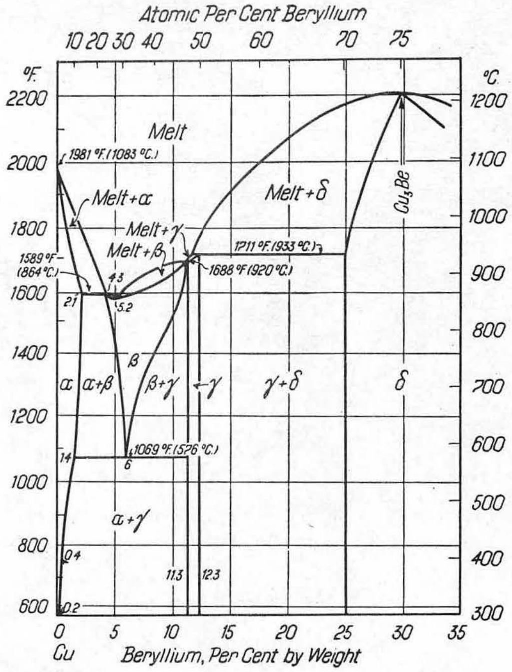
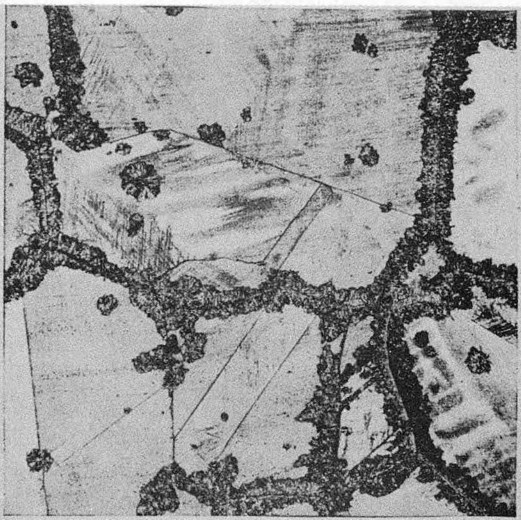


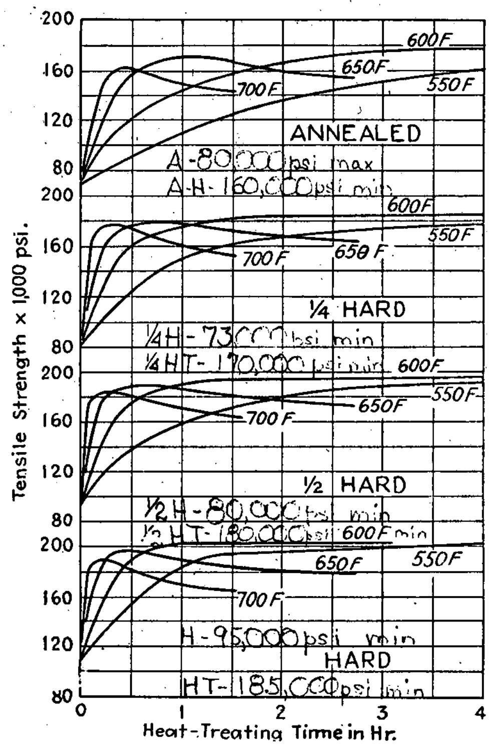
Fig. 33



Microstructure of Cu-Be alloy (1.97 % Be, 0.03 % Fe, no Ni) showing band of rapid precipitation at grain boundaries. Quenched from 820°C., aged 2 hr. at 325°C. ×75. (*C. S. Smith.*)

ZN263

Fig. 34



Typical age-hardening curves for beryllium copper (25 Alloy) strip.

Fig. 35