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An Investigation of the Age-Hardening of Copper with Nickel-Boron Compounds

Robert I. Moreen

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NICKEL-BORON COMPOUNDS

by

Robert I. Moreen

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of
the Requirements for the Degree of
Bachlor of Science in Metallurgical Engineering

Montana State School of Mines
Butte, Montana
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INTRODUCTION

Boron is an element whose metallurgical possibilities have never been fully investigated. The principal reason for this fact seems to lie in the difficulties encountered in preparing elemental boron and its various intermetallic compounds.

In many respects it closely resembles carbon and silicon, to the right of it in the periodic table. Due to the metallurgical usefulness of many of their alloys, there is some justification for believing that boron might possess similar utility. Many intermetallic compounds of silicon and carbon, when introduced into metals in comparatively small amounts, will cause them to age-harden. Since nickel silicide will age-harden copper, it appeared likely that nickel boride might have a like effect on it due to the already mentioned similarity of silicon and boron.

Our first problem was to obtain a relatively pure form of boron. A study of chemical trade catalogues revealed that it sells for one dollar a gram, and thus any
possibility of purchasing it was completely eliminated. Considerable time and research was expended on extracting a reasonably pure boron from boric acid. Several alloys with nickel were made, which have been studied by Mr. Willard M. Boam, my collaborator on the first portion of the problem.

I attempted to form a nickel-boron compound by fusing boron and nickel together. Two percentages of the resulting product were introduced into copper and the effects of solution and aging heat treatments on these have been investigated.

Elemental boron has few commercial applications as yet, although naturally occurring borax and borates are widely utilized. A few of the borides are used as special deoxidizers and scavengers in certain alloys. Boron carbide is a very hard abrasive, excelling silicon carbide, tungsten carbide, artificial aluminous abrasives, sapphire and all known abrasives except the diamond in hardness.

THEORY OF AGE-HARDENING

As stated by Paul D. Merica, it has become evident in the last few years that the metallurgist's power to improve the properties of alloys by heat-treatment is much greater than it was formerly supposed to be. At one
time it was believed that the only way to alter the mechanical properties of metals was by mechanical working and annealing procedures of limited application.

Today in consequence of the discovery of the phenomenon of "age-hardening", we are familiar with many alloys which are hardened by heat-treatment alone.

Age-hardening of this sort occurs only in alloys of the solid solution type. The alloy must contain a hardening constituent, which can be a metal or a metal compound, of which the solubility in the base alloy is greater at higher than at lower temperatures. The solid solution, saturated at higher temperatures with respect to this hardening constituent becomes super-saturated and unstable at lower temperatures as the metal is rapidly cooled. During the process of decomposition of this unstable solution, occurring gradually at lower intermediate temperatures, the alloy age-hardens.

In this way strength and hardness values may be developed in many non-ferrous alloys, comparable with those of heat-treated steel. For example the hardness of copper may be increased from 35 Brinell in the annealed condition to 400 Brinell in the 2.5% beryllium-copper alloys.

Wilm, working in Germany in 1906, first noticed
this type of hardening, in copper-aluminum alloys, containing magnesium and manganese. Although he never offered any reasons for this hardening, he developed the composition of duralumin, approximately as it remains to this day. Duralumin consists of 4.0% copper, 0.5% magnesium, 0.5% manganese, and 95% aluminum.

In 1919 Merica, Waltenberg and Scott presented a theory to explain the age-hardening of duralumin. This theory had four fundamental features, as follows:

1. Age-hardening is possible because of the solubility-temperature relation of the hardening constituent in aluminum.

2. This hardening constituent is CuAl₂.

3. The hardening is caused by the precipitation of this in some form other than that of atomic dispersion, probably in fine molecular, colloidal, or crystalline form.

4. The hardening effect of CuAl₂ in aluminum was deemed to be related to its particle size in the manner indicated in the graph of figure 1.

The optimum effect upon the hardness of aluminum was considered to be exerted when the CuAl₂ was critically dispersed in the form of particles having an average linear
size lying somewhere between that of atoms and that of about $10^{-5}$ cm.

Figure 1

Many alloys will age at room temperature, while others will only harden at higher temperatures. The rate of hardening will be increased at higher temperature, but if the alloy is held too long at these temperatures, the hardening will often be followed by subsequent softening, known as "over-aging". This seems to be due to the minute precipitated particles coalescing into larger particles, whose size is greater than the critical size.
As the temperature is lowered, the instability of the solid solution decreases. At first glance it seems strange that some alloys will age-harden at elevated temperatures, but not at room temperatures. However, as the temperature falls, the diffusion rate falls and may become too slow for particles to coalesce at room temperature and precipitate.

There is apparently no question that the atomic changes occurring during hardening and causing it are the direct result of the instability of the supersaturated solid solution and its decomposition in some manner during aging, but the nature of this decomposition is in doubt.

Objections to This Theory

In the case of duralumin there is no microscopic evidence of any precipitation of CuAl₂ particles below an aging temperature of 200°C, although it is entirely possible that there may be particles formed having diameters less than 10⁻⁵ centimeters, which is the smallest resolvable size that can be seen with the microscope.

At higher temperatures, there is no question that the aging is accompanied by the actual precipitation of CuAl₂ in particles of fine dispersion.
The evidence is very convincing that below 150° C. no precipitation in the ordinary sense takes place of discrete crystallling particles of CuAl₂. At these temperatures, hardening is completed before any precipitate appears and we must accept the conclusion that age-hardening in this alloy and in age-hardening alloys in general may also occur in consequence of some structural alteration other than the precipitation of excess solute.

Age-hardening develops gradually and requires time for its consummation, whatever its mechanism. At high temperature this time is certainly occupied by the diffusion of copper atoms. It is also natural to assume that diffusion occurs at room temperatures. Merica believes that the diffusion of the copper atoms plays an important part in all aging⁶, but speculates on the direction of diffusing, for they could migrate into several types of groups.

It is most natural to assume that they diffuse to positions that they might occupy just prior to atomic rearrangement and precipitation as crystalline particles of CuAl₂, and this is the assumption favored by most evidence, although there have been many investigators who believed differently. Merica believes these atoms assemble in ran-
dom groups on the duralumin and not the CuAl₂ lattice. This hypothesis is supported by the fact that even at 200 °C aging is practically complete, even before precipitation of CuAl₂ begins, suggesting that some preparation is made for precipitation by diffusion.

**Hardening by Distorted Groups or "Knots"**

We may picture these groups or lattice regions so formed by diffusion, as having local concentrations of copper atoms equal to or less than that required for the formation of a CuAl₂ lattice. Their concentration might vary, however, from center to periphery of the groups, which might vary in size and shape, containing at least two copper atoms, but not as many as are required to form a crystalline nucleus, which in the case of CuAl₂ would require four copper atoms.

In consequence of the local crowded condition of copper atoms on the lattice, which cannot hold them in equilibrium, it will be much distorted in the immediate region. Atomic arrangement in different groups probably represents degrees of transition from the aluminum lattice to the lattice of CuAl₂. Merica calls these groups "knots" and believes they are sufficiently rough and distorted so as to cause slip and deformation resistance
quite effectively in accordance with the "slip interference theory" of Jeffries and Archer. They are effectively hard and may be considered to act substantially as crystalline particles of CuAl₂ would act could they be formed in the same locations.

According to these ideas, then, not only can finely dispersed particles harden a metallic matrix, as they indeed do during the high-temperature aging of duralumin and other alloys, but hardening can be similarly effected by finely dispersed groups of such "knots" or "pseudo particles". Hardening can likewise be effected in any transition state between these two. Therefore, in duralumin aged at room temperature and in some other cases, it is not the crystallizing particles, themselves, but their "embryos", which actually occasion age-hardening.

This theory cannot be proved and in fact has some serious objections. In the first place, x-ray study of duralumin alloys does not reveal any evidence of lattice distortion, but it is well-known that in certain cases x-rays seem to be remarkably tolerant of some forms of lattice distortion. Also from one viewpoint, such a diffusion taking place would seem to be proceeding towards lattice distortion and not away from it, which is the usual
Incubation Period of Age-Hardening Alloys

Freshly quenched duralumin does not begin to harden immediately at any temperature of aging. However, during this period there are other indications of activity, as changes in the electrical resistivity and in the specific volume. Time is probably required for diffusion to proceed far enough to cause noticeable hardening.

Other Alloys

There are quite a few other age-hardenable alloys, which exhibit no change in the microstructure on hardening, but there are also many which do show some evidence of change. However, even in those which show visible evidence of change, there are certain peculiarities, common to the other type, and Merica believes that the mechanism is similar. An incubation period is noticed in several of the ones, having a visible change, similar to the one noticeable in the duralumin alloys.

Relations Between Constituents and Alloy Character

Some relations seem to exist between the age-hardening response and the character of the alloy system and its two components, solvent and solute. Most systems
will age-harden to a degree, approximately equal to the degree of hardness, obtained with mechanical working, but this is not the case in certain others as some will not harden as much, and a notable few will age-harden greatly in excess of this hardness.

As a somewhat general rule the hardening constituent is harder than the base metal, but there are cases in which it is softer. These are pertinent to the principle, postulated by Archer and Mehl that the potency of a hardening constituent need not depend on its average mechanical properties, but is primarily determined by the effectiveness of its dispersed particles in resisting or preventing slip in the host lattice with a large volume of these particles being more effective than a small volume.

**Change of Metallic Properties with Aging**

Tensile strength and hardness may or may not increase in direct proportion to one another. The plasticity decreases as the tensile strength and hardness increases. The endurance limit does not increase as rapidly as the tensile strength and hardness. Age-hardened alloys exhibit remarkable strength at elevated temperatures within the age-hardening range, showing considerable resistance to "creep". In fact many alloys continue to harden over a very
long period of time at high temperatures. The amount of hardening constituent is often so small that it does not materially affect the external properties of the base metal, especially the corrosion resistance.

The greatest fault of age-hardenable alloys is the tendency for inter-granular corrosion and embrittlement to occur, and is the reason that duralumin is sometimes clad with aluminum.

The addition of other elements may also affect the aging properties of duralumin and other age-hardening alloys. Adding iron retards the room-temperature aging of pure copper-aluminum alloy, whereas that of magnesium or of lithium accelerates it, and restores the capacity of iron-bearing copper-aluminum to age-harden at room temperatures. These elements, however, do not alter the velocity at any particular temperature.

BORON

History of Boron

Boron's history begins with the use of the salt "borax" during medieval times. When this use began is not known. The name "borax" is believed to have been derived from the Moorish word, "borras", which was de-
rived from the Arabian or Persian word "borak", meaning white. The Arabians, some Greek alchemical writers and chemists of the middle ages included nitrum, natron and borax under the names "bauracon, borach, baurak and baurach". When it was found that borax was much different from nitron, the term "baurach" was reserved for this salt.

During the middle ages there was a great deal of traffic in borax, which was imported to Europe from central Asia, through Constantinople and Venice. At this time it was called "tincal" or "tincar".

The term "baurax" was used by Raymund Lully and "baurach" by Roger Bacon. G. Agricola was wrong in many of his statements about boron. He said that chrysocolla—chryos, gold; colla, solder—of the ancients was borax. In the first century of our era, Pliny referred several times to the name, "chrysocolla", under which he seems to have included a gold solder, a copper ore, and a green pigment. Pliny made a statement that the chrysocolla, used as a gold solder was made from verdigris, nitrum, and urina. G. Agricola then argued that since borax is used to solder gold, that it and Pliny's chrysocolla were one and the same thing.

Some extraordinary guesses were made near the be-
ginning of the eighteenth century as to the nature of borac. A. J. Zwelfer regarded it as natural fixed alkali; G. Homberg as a "sel urineux mineral", and J. J. Becher, as a compound of the "universal acid" with a "vitrifiable earth". This confusion was partly the result of observations on the impure tincal which gave on distillation or combustion empyreumatic and ammoniacal products, derived from organic impurities, which were not recognized as accidental and foreign to the salt, but were considered to be inherent constituents of borax.

In 1702, G. Homberg heated borax with ferrous sulphate, and obtained a product, boric acid, which on account of its medicinal properties, was designated "sal sedativum". It came to be called by many names. It was later shown that boric acid could be obtained by treating borax with many acids in place of ferrous sulphate.

J. H. Pott found that the salt imparts a green color to the flame of burning alcohol. It was this coloration that led him and other chemists to assume that copper is an essential constituent of borax.

With the introduction of anti-phlogistic chemistry, the nature of borax became clear; "sal sedativum" was recognized as an acid and called boric or boracic acid. In
August, 1807, H. Davy electrolyzed moist boric acid and obtained a dark-colored combustible mass at the negative pole, and the following year he obtained a similar product by heating potassium with boric acid in a gold tube. Toward the end of 1808, he examined the properties of the dark product, and concluded, "from all analogy there is strong reason to consider the boracic basis as metallic in its nature, and I venture to propose for it the name of "boracium". In 1812 this same Humphery Davy stated that this element was more analogous to carbon than any other substance and hence proposed "boron" as a more exceptional name.

Properties of Boron

Just what the exact physical and chemical properties of pure boron are, no one can certainly say, because much of the knowledge on it has been based on none too pure samples. As produced, amorphous boron is pale brown, grayish-brown or bright-maroon, and stains the fingers.

Boron is classed as either a non-metallic or a metalloid. It is the fifth element in the periodic scale, lying midway between carbon which it closely resembles and beryllium and above aluminum. Its atomic weight is 10.82. Its specific gravity exceeds 1.84. A crystalline form has been claimed by many investigators, but most men\(^1\) think
that this is composed of a solid solution of $\text{AlB}_2$ and boron. This material is a black solid, having a specific gravity of 2.34 to 2.64. It is one of the hardest known materials, being only slightly softer than the diamond. It melts at 2,000$^\circ$ C. With a rise in temperature, the electrical conductivity of these crystals rapidly increase.

Boron is a non-conductor of the electric current, infusible or only fusible at some very high temperature, and is diamagnetic. At 1200$^\circ$ C. it has a considerable vapor pressure.

It is insoluble or just slightly soluble in water; insoluble in alcohol, ether, solutions of caustic alkalis, and hydrochloric acid; and soluble in cold nitric acid, when it is soluble in hot sulphuric acid. Owing to its finely-divided condition it is somewhat likely to take fire at room-temperature, unless an attempt is made to consolidate it. If heated above 300$^\circ$ C. it burns with a reddish light.

Amorphous boron unites more readily with the metalloids than it does with any of the metals, and it has a strong affinity for oxygen, sulphur, fluorine and chlorine. It is a more energetic reducing agent than carbon or silicon because it decomposes the oxides of these elements at a
red heat. Its general chemical properties resemble those of carbon more closely than those of silicon. Indeed, boron resembles no other element so much as it does carbon.

**Occurrence of Boron**

Boron is not a particularly rare element. Workable deposits of boron minerals are quite uncommon, but it has a wide distribution in small amounts. According to Clarke, the 10-mile crust, the hydrosphere and the atmosphere of the earth contain 0.001% of Boron.

In nature, boron is never found in the uncombined or elementary state. Especially in regions of former or present vulcanism, it occurs in the form of boric acid and borates. Also it is an essential constituent of many silicate minerals, such as tourmaline and datolite, etc.

In old Lake beds, as in the Great Basin of California and Death Valley, borates, particularly colemanite \((Ca_2B_2O_11\cdot5H_2O)\), occur in bedded deposits with other sedimentaries, such as gypsum, limestone and shales. These deposits are believed to have originated from the action of boric acid solutions or vapors upon these rocks. The borax marshes of California, Nevada and Oregon contain ulexite \((2CaO\cdotNa_2O\cdot5B_2O_3\cdot16H_2O)\) and borax \((Na_2O\cdot2B_2O_3\cdot10H_2O)\), probably derived from the leaching of colemanite at higher
The "soffioni" or fumaroles of Tuscany, Italy are an important source of boric acid. Jets of steam, carrying boric acid emerge from the ground, condense in lagoons and deposit "sassolite" (naturally-occurring boric acid). In various places boron minerals are deposited by hot springs. Boracite of marine origin is found in the complex salt deposits of the Strassfurt district of Germany.

Boric acid is found minutely in some animal tissues. Living matter probably contains about one part of boron in 100,000,000 parts¹.

The southwestern United States contains the world's largest deposits of boron minerals. In general the minerals are readily available with mining costs being low. As a result of the Bureau of Mines investigations, it is quite probable that the colemanite in these deposits can serve as a source of metallic borides and calcium borate, which is used in the ceramics industry⁴.

**Metallic Borides**

Boron forms compounds with several metals and metalloids, but as most of these are quite difficult to make, possible metallurgical uses for them have only been slightly investigated.
There are some which are used to a limited extent for the deoxidation and degasification of molten non-ferrous metals. These are calcium boride, \((\text{CaB}_6)\), manganese-silicon boron, manganese-calcium-copper boron (about 85% copper and 2% boron), and manganese boride \((\text{MnB}_6)\). These boron alloys are used mostly in the brass and bronze industries.

Boron carbide, zirconium boride, tantalum boride and titanium boride are among the hardest materials known, and it is to be expected that some of these may find utility in the manufacture of bearings and the like.

Remarkably strong steel has been made, using 0.5 to 2% boron, and ferroboron has been used to a limited extent in a few special steels, but the exact qualities have not been actually determined that it imparts to them.

Practically all commercial borides are made in electric furnaces. Most cannot be tapped molten, and the furnace must be torn down after each production.

Due to cheap power available from Boulder Dam, the United States Bureau of Mines has been conducting work on the production of calcium boride by the electrolysis of molten mixtures of lime and boric oxide. Boulder Dam colemanite deposits are quite suited to electrolytically pro-
duce calcium boride, a compound, which already has a limited commercial use and, one, which can be used to produce other borides and boron for the extensive investigation that the Bureau of Mines is beginning on their metallurgical possibilities.

Miles C. Smith reports that the additions of mixtures of metallic boride crystals and nickel to gray cast iron, mild low-carbon steel and copper cause the corrosion and wear resistance of these metals to be increased greatly beyond all expectations. Although he is very secretive concerning the details of the nickel boride mixtures and manufacture, he states that they are made of a mixture of a high-melting point boride and a much lower-melting point boride which are added to nickel, in various percentages to form what he calls a "mother", which is easily introduced into most metals. He claims that copper acquires some very interesting properties, when alloyed with this in various percentages.

With 10% to 25% added, copper becomes quite hard and acquires greater corrosion resistance, and its density increases 5 to 7.

Nickel forms several borides more or less easily. Nickel boride (15.56% boron) is the most easily made under
ordinary conditions. As prepared pure, it forms into brilliant prisms which are several millimeters long, magnetic and about as hard as quartz. Their specific gravity is 7.39. They are attacked by chlorine at a dull red heat and by bromine at a higher temperature. Fused carbonates, nitrates, hydroxides and alkali chlorates dissolve and decompose them; water vapor at a dull red heat converts them into oxides and boric acid, and acids concentrated and dilute, attack them with varying degrees of readiness. It dissolves quickly in HNO₃, not at all in HCl and only in H₂SO₄ if heated. It can be made by fusing the constituents in an electric furnace in crucibles brasqued with powdered boron⁰.

Nickel diboride (NiB₂) also forms quite easily, when its constituents are fused together in an electric furnace. If the excess nickel of the resulting product is removed electrolytically in a nickel chloride solution, the pure compound remains, consisting of small slender, yellow, acicular crystals¹, which are violently attached by nitric acid, slowly by hot hydrochloric acid⁹, and are slightly oxidized by long exposure to air. It is somewhat softer than nickel boride.

As indicated on the figure (Fig. 2), there are two other compounds formed between nickel and boron in this
range, nickel hemiboride \((\text{Ni}_2\text{B})\) and nickel trihemi-
boride \((\text{Ni}_2\text{B}_3)\). \(\text{Ni}_2\text{B}\) may be
prepared by heating the
constituents in a stream
of hydrogen passing thru a
porcelain tube. Figure 2
is the freezing-point
curve of mixtures of nick-
el containing up to 20%
boron.

The compound \((\text{NiB})\) is indicated as having a melt-
ing point of 1020° C. These alloys are non-magnetic, un-
less they contain free nickel.

LABORATORY WORK

The Preparation of Boron

The preparation of elemental boron is reported
by many investigators, but it is quite probable that it has
never been produced in an absolutely pure form\(^4\) owing to its
strong reactivity with carbon, oxygen, nitrogen, carbon mon-
oxide, carbon dioxide, most metallic oxides and the halogens.

J. L. Gay Lussac and L. J. Thenard in 1808 prepared a very impure boron by fusing boric acid with potassium in a tube of copper, iron, platinum or glass. The product was boiled with dilute hydrochloric acid, washed with water, and dried at a gentle heat. H. Davy and R. D. Thompson made an impure boron by fusing boric acid with sodium in the presence of sodium chloride.

H. Moissan stated that heating boric anhydride with the theoretical amount of magnesium results in the formation of various magnesium borides, but that if a large excess of boric anhydride is used, the results are quite different. In this case amorphous boron is formed in the presence of magnesium boride.

The United States Bureau of Mines in its electrometallurgical laboratories at Boulder City, Nevada has been conducting experimental work with the object of producing relatively pure boron, cheaply. By means of flotation and the recrystallization of flotation concentrates in hot solutions, an almost pure boric acid has been obtained from colemanite (2CaO·3B₂O₃·5H₂O), which exists in large quantities near Boulder Dam. Other work on the prob-
Problem of producing pure boric acid from this mineral has been conducted here\textsuperscript{4}.

Their efforts to produce a pure boron have involved the decomposition of various boron compounds, rather than the reduction of the oxide directly with some reducing agent. This experimentation, although as yet incomplete and inconclusive, indicates that the reduction of magnesium boride with boron trichloride under proper conditions may prove to be the means of making a very pure product, inexpensively.

Magnesium boride was produced by the reaction between a mixture of boric oxide and powdered magnesium in a magnesia crucible under an atmosphere of helium. A maximum yield was obtained when equal parts of the constituents were heated together at a temperature of 1050\textdegree{} C. To obtain boron the boride was reduced with boron trichloride at a temperature of 750\textdegree{} C., under a pressure of 115 pounds to the square inch. Although the boron produced so far has not been pure, there is definite promise that in the future high-grade material may be made.

**Laboratory Preparation of Boron**

Boric acid was heated in assay crucibles to a bright red heat to drive off the water. During heating, it
underwent several changes, becoming at first quite fluid, and later at a bright red heat, changing to a pasty mass, which was probably tetraboron trioxide (\(\text{B}_4\text{O}_3\cdot\text{2H}_2\text{O}\)). When bright red this changed to a clear quiescent liquid. We rapidly poured the liquid, which was very viscous, onto a porcelain plate. Because it solidified in a very few seconds, there was little tendency for it to stick to the plate, if it was worked with a glass rod. The liquid coalesced into a tough glass, which was very tough and resistant to attrition, a decided disadvantage because boric tri-oxide will revert to boric acid if handled too long in the air, as it is very hygroscopic.

On a batch of the oxide, which I made quite recently, I used a somewhat different technique of manufacture. Having found by experience that the molten liquid in the crucible solidifies quickly, I decided to try pouring it over a large surface. After thoroughly cleaning the large crushing table in the assay laboratory, I poured the liquid on it so as to form little strings over the entire surface. They hardened so rapidly that they were solid before they touched the surface, eliminating the possibility of any appreciable amount of contamination from it. Gathered up, it was possible to crush them in a few seconds.
to a high degree of fineness.

To produce elemental boron we followed the method outlined by H. M. Moisson with some modifications of technique found necessary. Due to the extremely small yield, boron had to be manufactured three times.

If magnesium and boric oxide are mixed together in the theoretical proportions and heated, they will react to form magnesium boride, but if the magnesium is heated with a very large excess of boric anhydride, a certain amount of the oxide will be reduced to boron, in addition to the magnesium borides formed.

The first time we intimately mixed 30 grams of our prepared, powdered boric oxide with 10 grams of magnesium, and heated the mixture in a crucible, brasqued with a mixture of carbon and titanic oxide to prevent the formation of boric nitride, as recommended by H. Moisson. There was little possibility of boron reacting with carbon, because boron carbide will only form above 2000° C.

The mixture was placed in the muffle, became molten, and a violent reaction occurred in the material, which swelled up and glowed at a white heat. The crucible had to be broken to remove the brown, porous solid filling it.

This was boiled in a beaker with hydrochloric a-
acid and water for several hours until it had all gathered as a sludge in the bottom, which was filtered and washed. This was boiled for a long time with hydrochloric acid, filtered and successively washed several times with boiling water, diluted hydrochloric acid and solutions of potassium hydroxide in alcohol. The remaining residue was placed in a beaker, containing a mixture of hydrochloric and hydrofluoric acids, boiled for an hour, filtered and washed as before. Moisson's product at this point contained (94-95)% boron, (2.3-3.75)% magnesium and (1.2-1.6)% insoluble matter. He states that this must be fused with borax if any more of the contained magnesium is to be removed.

Our material at this point weighed five grams, which was fused with one hundred fifty grams of borax. The resulting fused glass was given the same leaching treatment as the product of the first fusion. Washing the borax out of the boron was done with great slowness and difficulty, because it clogged the filter.

The boron yield was found to be extremely small. The final product weighed slightly more than two grams. We had expected it to be small, but this was even smaller than anticipated.
For a second charge we weighed out ninety grams of boric oxide and thirty grams of magnesium, following the same procedure as before, but we used boric acid in the second fusion, instead of borax as first used, finding it much easier to filter and wash out. From this batch we made about seven grams of boron. We mixed our borons together and analyzed the composite product for boron content by the "ethyl borate" distillation method, and found it to contain 96.3% boron. In addition a spectroscopic analysis was made of this product.

As indicated in figure 3, which is the spectrograph that was made, the chief impurities were copper and magnesium. Also present were minor amounts of calcium and silicon and traces of aluminum, barium and iron. Dr. S. R.
B. Cooke estimated that the boron contained between one and five per cent impurities as the result of a study that he made of the spectrograph. The purity of our boron was quite comparable to that of products by other men.

Just recently I again made boron, using a much larger charge. It contained two hundred forty grams of freshly-powdered boric oxide and eighty grams of magnesium. The boron yield this time was somewhat better on a percentage basis as thirty grams were produced. I believe that this was due to the larger charge and to the greater fineness of the boric anhydride in the charge.

Analysis of Boron

Chemical analysis, supplemented by spectroscopic analysis was used to analyze the boron produced; only the boron content was obtained chemically and the amounts of other constituents were estimated from the spectrograph made.

The boron was determined by the "ethyl borate" distillation method. This one depends upon the fact that borates of alkaline earths and alkalies will give up their boron in the form of the volatile methyl borate or ethyl borate, when they are distilled with absolute methyl alcohol or ethyl alcohol. The ethyl or methyl borate,
passed over lime in the presence of water, will be completely saponified, the liberated boric acid combining with the lime to form calcium borate, which may be dried, ignited and weighed, with the increase of the weight of the lime, representing the $\text{B}_2\text{O}_3$ in the sample.

This analysis was carried out in the apparatus, shown in figure 4. About one gram of pure calcium oxide was ignited to constant weight and transferred to the dry, Erlenmeyer receiving flask.

One-tenth gram of the boron was weighed out carefully, fused with six-tenth grams of potassium hydroxide, and dissolved in water. This solution was now treated with a few drops of litmus solution and the free alkali was neutralized with dilute hydrochloric acid, drop by drop. A drop of dilute sodium hydroxide solution was added and then a few drops of acetic acid. The slightly acid solution was transferred to the condenser, shown in the figure by means of the overhead funnel. The beaker was washed out with three 2 to 3 cc. portions of water. The paraffin was heated to not over $140^\circ$ C. and placed under the condenser, whose stopcock had been closed. The liquid in the retort was distilled into the receiver, containing the known amount of lime. After all the liquid had been removed, the
paraffin was lowered, allowing the condenser to cool. When cool, 10 cc. of ethanol were added to the residue through the funnel, the stopcocks were closed and the paraffin bath was set in place, and the contents were distilled. This process was repeated three times with ethyl alcohol. The contents of the condenser, which were now alkaline, were made distinctly acid by the addition of acetic acid. The distillation was repeated three more times with ethyl alcohol, using 100 cc. portions this time. The paraffin bath was now removed, the receiving flask was stoppered, and the contents were thoroughly mixed and set aside for at least an hour to allow saponification to take place of the ethyl borate. The contents were now poured into a porcelain dish and evaporated in a water bath, below the boiling point of the alcohol, because loss of boric acid will occur if the alcohol boils. The lime, adhering in the flask was dissolved by wetting its entire surface with a few drops of nitric acid, the flask being inclined and revolved to allow the acid to flow over the sides. The contents were transferred to the dish with a little water and the evaporation was repeated. During this stage, there was no danger of losing boric acid as all the alcohol had been removed in the first stage. The residue was gently
heated to destroy any calcium acetate that may have formed. The cooled borate and lime were taken up with a little water and transferred to the crucible in which the lime was heated and weighed. The material clinging to the dish was dissolved with a little nitric acid and washed into the crucible. The contents of the crucible were evaporated to dryness on the water bath, then heated very gently over
a flame, keeping the crucible covered, and finally heated more strongly. The heating was continued until a constant weight was obtained. The increase in the weight of the lime represents the amount of $\text{B}_2\text{O}_3$ in the sample.

**Analysis of Alloys**

When analyzing the nickel-boron alloys and the nickel boride, a different method was used to determine boron. Although it probably was not quite as accurate as the other method, it could be done much faster, once the end point colors were determined.

One-tenth gram samples were weighed out and dissolved in a small amount of nitric acid.

There was some difficulty putting the nickel-boron alloys into solution, but the nickel boride readily dissolved in the nitric acid, when a little water was added. To remove the nitric acid the solution was boiled with 20 cc. of 1:1 sulphuric acid until the white fumes of sulphur trioxide were evolved for several minutes. This was slowly cooled and water was cautiously added, until the solution was diluted to 150 cc. As there was a slight amount of iron and aluminum present, one gram of tartaric acid was added to prevent their precipitation as hydroxides. The solution was now just slightly alkaline with ammonium
hydroxide, and it was discovered that slightly better results were obtained if a drop of hydrochloric acid was added at this point. The solution was heated to nearly boiling, and 70 cc. of a 1% alcoholic solution of dimethylglyoxime were added for every tenth of a gram of nickel, estimated to be present. Ammonium hydroxide was added until the solution had the distinct odor of ammonia. The scarlet-colored nickel gyoxine rapidly precipitated at this point. After allowing it to stand for a few minutes, it was filtered through a tared Gooch crucible.

The precipitate was dried for an hour at a temperature of 120°C., and the crucible was weighed. The difference between this weight and the first weight of the crucible equaled the weight of C₈H₁₄N₄O₄Ni present, which contains 20.32% nickel.

The filtrate was saved for the boron determination. This determination takes advantage of the fact that boron reacts neutral to methyl orange, but is acid to phenolphthalein, and may be quantitatively titrated in the presence of mannitol or glycerol.

The filtrate was made slightly alkaline, methyl orange was added, and the filtrate was titrated with a normal solution of H₂SO₄, until the yellow color was replaced
by an orange red. Phenolphthalein and 50 cc. of glycerol, tested and found neutral, were added to the solution. The solution was titrated with tenth-normal sodium hydroxide, which had been standardized with carefully dehydrated boric oxide, until the color changed first to yellow and then very shortly to an orange-red, which was the desired end-point. Ten cc. of tenth-normal NaOH equaled 0.062 grams of H$_3$B$_3$O$_3$.

Important considerations in this analysis were to always have the solution at the same dilution, have the same amount of methyl orange and phenolphthalein present and observe the identical color changes as first determined on blank solutions of weighed amounts of boric acid, titrated until checks were obtained.

The alloys of copper and nickel-boride were treated in exactly the same manner except the copper was precipitated out with hydrogen sulphide after the samples were put in solution, just before the nickel analysis. The percentage of copper was obtained by difference.

**Preparation of Nickel Boride**

Of the several intermetallic compounds that nickel forms with boron, nickel boride (NiB) is the one most likely to form under the conditions, attainable in our
laboratory, and this was the one I undertook to make. The biggest obstacle to its manufacture in a pure form was the readiness of boron to oxidize at high temperatures.

This was prepared in an electric induction furnace, using alundum crucibles. A charge, containing one part powdered boron and four parts powdered nickel, was weighed out and intimately mixed. Although the theoretical amount of boron in NiB is 15.56%, I introduced a greater percentage into my charge, and thus made an attempt to allow for losses by oxidation and volatilization.

The induction furnace, partially filled with a block of charcoal, was heated up above 1455° C., the melting point of nickel before an attempt was made to introduce the charge. When the furnace was hot, the charge was poured in on a metal funnel, through spaces at the side of the charcoal. As was anticipated there was considerable loss of the boron, when it was introduced. Due to the high heat of the furnace the nickel very rapidly became molten and in a few minutes a quite active reaction occurred in the crucible. The charge was poured and it quickly solidified into metallic globules. When struck with a hammer, they shattered easily, being very brittle. This was a rather good indication that an intermetallic
compound may have been formed by the reaction in the charge.

The product was analyzed for nickel and boron, and the results were as follows:

Ni----87.48%.
B----12.23%.
Diff.- 0.29% (Possibly contained oxygen as boric oxide)
Total-100.00%.

As can be readily seen, the product had quite a bit less boron than the amount contained in NiB (15.56%). This gave rise to some speculation as to its nature in the alloy. As already indicated on figure 2, there are several compounds formed in the range between Ni2B, which contains 8.44% boron and Ni2B3, which contains 21.7% boron. However, of these, the only ones that seem likely to form under ordinary conditions are NiB and Ni2B1. In the section "Metallic Borides" on pages 20 and 21, I have already described the important characteristics of these intermetallic compounds. The alloy, formed, fitted the characteristics of NiB almost perfectly and those of Ni2B much less. It had a metallic lustre, was in the form of prismatic crystals, was insoluble in HCl, and was soluble in a somewhat dilute HNO3. Judging from these characteristics, it was likely to assume it was composed of NiB and
excess nickel.

I have made an assumption that the analysis difference of 0.29% represents contained oxygen, but this is admittedly only slightly more than a guess, but it is a guess based on a certain amount of evidence. It is quite possible that the analysis of boron may have been a little in error, because as before stated, the volumetric determination of boron is subject to a slight variance in results. When the copper-nickel-boride alloys, described in the next section, were examined under the microscope, a few bluish-colored dots were seen, which may have been oxide inclusions of boric oxide.

If the foregoing assumptions are correct, the alloy's analysis by compound constituents was as follows:

\[
\begin{align*}
E_2O_3 &\quad 0.42\% \\
NiB &\quad 77.80\% \\
Ni &\quad 21.78\% \\
\text{Total} &\quad 100.00\% 
\end{align*}
\]

It must be remembered, that even though the alloy had all the properties of NiB, there still could have been and probably were other nickel-boron compounds present in small amounts.

**Introduction of Nickel Boride to Copper**

Alloys were made of the nickel boride alloy and
copper. The constituents were weighed out in amounts, calculated to make one alloy, containing about 2% of the nickel boride alloy and a second one, containing about 4% of that substance. Both alloys were made exactly the same way.

Copper was first melted in the induction furnace. After the copper had become somewhat superheated, the nickel boride alloy was dumped into it and immediately dissolved, indicating that its melting point was much lower than the melting point of nickel, which would be true if it were composed principally of nickel boride.

Figure 5 illustrates the cast structure of alloy one, taken at 150 magnifications. Some dendritic segregation is noticeable, and although the photomicrograph doesn't reveal it clearly, a small amount of what I believed to be oxide inclusions was visible as little bluish-colored dots.

Figure 6 illustrates the cast structure of alloy 2, taken at 150 magnifications. Its cast structure was essentially the same as that of alloy 1. One rather unusual thing is noticeable in two places in the print and that is the inclosure of some grains by the boundaries of other grains. This phenomenon was visible here and there over
the entire surface of the alloy.

Alloy 1 analyzed as follows:

- Ni: 1.73%.
- B: 0.23%.
- Cu: 98.04% (by difference).

Total: 100.00%.

Assuming that all the boron was present as NiB, alloy 1's analysis by actual components follows:

- NiB: 1.48%.
- Ni: 0.48% (as excess).
- Cu: 98.04% (by difference).

Total: 100.00%.

Alloy 2 analyzed as follows:

- Ni: 3.72%.
- B: 0.51%.
- Cu: 95.77% (by difference).

Total: 100.00%.

And assuming as before that all the boron existed as nickel boride, alloy 2's analysis by actual components follows:
NiB—- 3.28%.  
Ni----- 0.95%. (As excess).  
Cu-----95.77%. (By difference).  
Total- 100.00%.  

The computation for NiB is of course correct only if it were one intermetallic compound of nickel and boron that was present.

500 grams of alloy were made each time with each alloy being cast in two molds.

Age-Hardening of Alloys

One casting of each of the alloys was placed in the furnace for a homogenizing annealing treatment, overnight at a temperature of 800°C. However, the addition of the nickel boride to the copper must have lowered its melting point, greatly, because they melted at that temperature. As no phase diagrams have been determined for the NiB-Cu system, nothing of this sort had been anticipated. Copper has a melting point of 1083°C. and NiB has a melting point of approximately 1020°C.¹.

The other portions of the alloys had been cast in cylindrical shapes, but I pounded them with a hammer and rolled them until they had been pounded very flat.

The work-hardened, flattened casting were both
annealed forty-eight hours at a temperature of 400\(^\circ\)C.,
until they showed appreciable softening and then were
given the following tests:

In the first test they were heated at a temper-
ature of 600\(^\circ\)C. in an attempt to give them a solution
heat treatment. This temperature was used because it
seemed a likely one, but as there was no knowledge of any
points on the phase diagram it was purely an experimental
try. After a four hour treatment, they were quenched in
cold water and their hardness was determined on the "Rock-
well Superficial Hardness Machine". They were allowed to
stand at room temperature for fifty hours with periodic
measurement of their hardnesses to determine if any age-
hardening would result after this treatment.

In the second test they were given the same so-
lution heat treatment at 600\(^\circ\)C. for four hours and
quenched in cold water. The aging effects at 100\(^\circ\)C. was
determined in a "Freas" electric oven over a period of fif-
ty hours with periodic hardness measurements.

Figure 7 is the photomicrograph of alloy 1 after
the solution heat treatment. Figure 8 is the photomicro-
graph of alloy 2 after the solution heat treatment. Fig-
ure 9 is the photomicrograph of alloy 2 after aging fifty hours at 100°C. 150 diameters was the magnification used.

In the third test they were given solution heat treatment at 600°C for sixteen hours and quenched in cold water. The four hour heat treatment had seemed sufficient, but they were left overnight at this temperature, as it was believed desirable to measure the hardnesses more frequently for a few hours for the next precipitation heat treatment tests, which were carried on at 150°C for twenty-five hours, with periodic measurements of hardness.

In the fourth test they were given a solution heat treatment at 600°C for sixteen hours and quenched in cold water. The aging effects at 175°C were determined in the "Freas" electric oven with periodic hardness measurements over a period of twenty-four hours.

Figure 10 is the photomicrograph of alloy 1 after the last solution heat treatment, taken at 200 magnifications. Figure 11 is the photomicrograph of alloy 2 at 200 magnifications. Figure 12 is the photomicrograph of alloy 2 at 250 diameters.

The solution heat treatments were made in a "Hoskins" electric furnace.
Figure 7

Figure 8
### SUMMARY OF ANALYSES

#### Boron

<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>B</strong>------96.8%</td>
</tr>
<tr>
<td><strong>Mg Cu</strong>- 3.2% (Diff.)</td>
</tr>
<tr>
<td><strong>Ca Si</strong>- Trace</td>
</tr>
<tr>
<td><strong>Total</strong> - 100.0%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Corresponding to:</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td><strong>Ca Si</strong>- Trace</td>
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<tr>
<td><strong>Total</strong> - 100.0%</td>
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#### Nickel Boride Alloy

<table>
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<tbody>
<tr>
<td><strong>Ni</strong>------87.48%</td>
</tr>
<tr>
<td><strong>B</strong>------12.23%</td>
</tr>
<tr>
<td><strong>Diff.</strong>-- 0.29% (as B$_2$O$_3$)</td>
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<tr>
<td><strong>Total</strong> - 100.00%</td>
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</table>

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</thead>
<tbody>
<tr>
<td><strong>B$_2$O$_3$</strong>-- 0.42%</td>
</tr>
<tr>
<td><strong>NiB</strong>---- 77.80%</td>
</tr>
<tr>
<td><strong>Ni</strong>------21.78%</td>
</tr>
<tr>
<td><strong>Total</strong> - 100.00%</td>
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#### Alloy No. 1

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<tbody>
<tr>
<td><strong>Ni</strong>------ 1.73%</td>
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<tr>
<td><strong>B</strong>------ 0.23%</td>
</tr>
<tr>
<td><strong>Cu</strong>----98.04% (Diff.)</td>
</tr>
<tr>
<td><strong>Total</strong> - 100.00%</td>
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</table>

<table>
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<th>Corresponding to:</th>
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<tbody>
<tr>
<td><strong>NiB</strong>---- 1.48%</td>
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<tr>
<td><strong>Ni</strong>------ 0.48% (Excess)</td>
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<tr>
<td><strong>Cu</strong>----98.04% (Diff.)</td>
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#### Alloy No. 2

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<td><strong>Ni</strong>------ 3.72%</td>
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<td><strong>B</strong>------ 0.51%</td>
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<tr>
<td><strong>Cu</strong>----95.77% (Diff.)</td>
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<td><strong>Total</strong> 100.00%</td>
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</table>

<table>
<thead>
<tr>
<th>Corresponding to:</th>
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<tbody>
<tr>
<td><strong>NiB</strong>---- 3.28%</td>
</tr>
<tr>
<td><strong>Ni</strong>------ 0.95% (Excess)</td>
</tr>
<tr>
<td><strong>Cu</strong>----95.77% (Diff.)</td>
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<td><strong>Total</strong> 100.00%</td>
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### TABULATION OF HARDNESS MEASUREMENTS

**Alloy No. 1**

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<tr>
<th>Treatment</th>
<th>15-T Rockwell Superficial Hardness</th>
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<tr>
<td>Work-hardned</td>
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<tr>
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**Treatment No. 1**

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**Aging at 100°C.**

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**Treatment No. 2**

<table>
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<th>16 hr. solution heat treatment at 600°C.</th>
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**Aging at 150°C.**

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### Treatment No. 3

16 hr. solution heat treatment at 400\(^\circ\) C.

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Aging at 175\(^\circ\) C.

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Alloy No. 2

15-T Rockwell Superficial Hardness

As cast 51
Work-hardened 80
Annealed 48 hr. at 400° C. 71

Treatment No. 1

4 hr. solution heat treatment at 600° C. 55

Aging at Room Temperature

Hours

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Treatment No. 2

4 hr. solution heat treatment at 600° C. 57

Aging at 100° C.

Hours

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Treatment No. 3

16 hr. solution heat treatment at 600° C.

Aging at 150° C.

<table>
<thead>
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<th>Hours</th>
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<tbody>
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Treatment No. 4

16 hr. solution heat treatment at 600° C.

Aging at 175° C.

<table>
<thead>
<tr>
<th>Hours</th>
<th>56</th>
</tr>
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<tbody>
<tr>
<td>0.75</td>
<td>64</td>
</tr>
<tr>
<td>1.5</td>
<td>65</td>
</tr>
<tr>
<td>2.5</td>
<td>61</td>
</tr>
<tr>
<td>3.5</td>
<td>62</td>
</tr>
<tr>
<td>4.5</td>
<td>60</td>
</tr>
<tr>
<td>5.5</td>
<td>61</td>
</tr>
<tr>
<td>24</td>
<td>61</td>
</tr>
</tbody>
</table>
Figure 15
COMPARATIVE AGING CURVES OF ALLOYS ONE AND TWO

Aging 20% time 25 in 30 hours 35
DISCUSSION

As clearly revealed by figure 13, alloy No. 1 hardened to the maximum value after a sixteen hour solution heat treatment at 600°C and a 3½ hour precipitation heat treatment at 150°C, and rapidly overaged after this time. 175°C apparently was too high a temperature to conduct precipitation heat treatment as the alloy quickly reached a maximum value and overaged. At 100°C the aging was a great deal slower, but the hardness attained was only 1 point below the maximum. Although time didn’t allow its determination, there may have been a temp. somewhere between 100°C and 150°C at which the greatest hardening would have occurred.

Figure 14 indicates that alloy No. 2 reached its maximum hardness of 70 after a 4 hour solution heat treatment at 600°C and a 24 hour precipitation heat treatment at 100°C. This was the greatest hardness obtained on either of the two. In contrast to alloy No. 1 there was no overaging of alloy No. 2 at this temperature. But when given a precipitation heat treatment at 150°C, there was considerable less hardening and overaging started after 2½ hours. But as with the other alloy, there may have been a temperature, lying between 100°C and 150°C at which the
greatest hardening would have occurred.

If there had been more time, it would have been desirable to have tried different solution heat treatment temperatures in an attempt to determine the best one.

When work-hardened, alloy 1 had a hardness of 82, while alloy 2 had a hardness of 80. Because many but not all age-hardenable alloys will become as hard, during aging, as they will by working, the best possible conditions may not have been achieved. If further investigation should actually cause these alloys to be useful, the phase diagram of this system would have to be determined.

After the second solution heat treatment, the two alloys were still extremely fine-grained as seen in figures 7 and 8, the photomicrographs of alloys No. 1 and 2, respectively, immediately after quenching. Figure 9 was taken after alloy 2 had attained its maximum hardness of 70 in an attempt to determine if any precipitation had occurred, but so far as brought out by the etching, no evidence of this is visible.

There was some grain growth between the second solution heat treatment and after the fourth heat treatment of alloy 2 as visible in figure 11. Figure 12 was taken of this alloy after being overaged at 175° C. for
five hours at a magnification of 250 diameters, and I believe that the grain boundaries contain precipitated particles, that have undergone grain growth.
CONCLUSIONS

As a result of the experimental work the following conclusions were made:

1. Copper is appreciably hardened by the addition of alloys, containing compounds of nickel and boron, if the proper conditions are maintained.

2. The amount and rate of this hardening critically depends upon close temperature control.

3. Varying the composition of the copper-nickel-boron alloy causes a considerable differing of the conditions under which it age-hardens. The conditions under which the copper age-hardens considerably depend upon the amount of nickel-boron added.

4. The melting point of copper was lowered to a considerable but undetermined degree by the addition of the nickel-boron alloy, indicating a eutectic or peritectic reaction occurs between copper and the added component or components.

5. The principle compound in the nickel-boron alloy that age-hardens the copper is probably NiB.
ACKNOWLEDGEMENTS

I wish to take this opportunity to thank Prof. John P. Spielman and Mr. Bernard Cullity of the metallurgical department for their advise, assistance, and guidance without which this work would have been impossible. Dr. S. R. B. Cooke receives my gratitude for the spectroscopic analysis he ran on the boron, confirming our analytical results. The assistance of Miss Mae Stewart, who helped edit and type the manuscript was invaluable.