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A MAGNETIC RESONANCE STUDY OF
AGE HARDENING IN CU-BE ALLOYS

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CHAPTER I - INTRODUCTION

1.1 Physical Properties and Age-Hardening of Beryllium-Copper Alloys

One of the conditions which is necessary, although not always sufficient, for an alloy to be susceptible to age-hardening is that the limit of solubility of the alloy metal should decrease with decreasing temperature. This requirement is fulfilled by the copper-beryllium alloys as exhibited by the phase diagram,¹ Figure 1. Consequently, the copper-beryllium alloys may be age-hardened to a very considerable degree. It will be seen that 2.7% beryllium (by weight) should be in solid solution at 866°C and that it should precipitate the β phase above 605°C and the β' phase at lower temperatures. In practice the major copper-beryllium alloy that is used contains 2% (by weight) beryllium and about 0.25 wt.% cobalt; precipitation is carried out at about 350°C for a period of 2-3 hours. The tensile strength attainable by this treatment is 200,000 psi, combined with 2.8% elongation.

Pure beryllium has a hexagonal close-packed structure with $a = 2.8 \text{ kX}$ and $c = 3.58 \text{ kX}$, while Cu is a fcc metal with a lattice parameter of 3.6 kX at 20°C. The equilibrium room-temperature phases of the system are α , β' (formerly designated γ) and δ , with α having a face-centered cubic structure with a lattice parameter of 3.566 kX at 2.1 wt.% Be, β' a body-centered cubic structure with the CsCl type of ordering and a lattice parameter of 2.70 kX , and δ being a cubic (Mg_2Cu -type) with the lattice parameter ranging from 5.940 to 5.887 kX .² The atomic size factor of Be with respect to Cu is 12% and Be is a substitutional solute in this binary system. Be is a divalent species as opposed to the monovalent Cu.

Figure 1 The copper-beryllium phase diagram from Hansen, The constitution of binary alloys, p. 282.

Early work on the age-hardenability of the Cu-Be alloys was conducted by M. G. Carson who tested alloys containing 0.3 wt.%, 1.2 wt.% and 1.7 wt.% beryllium.³ Although the latter alloy, as will be shown later, is considerably age-hardenable, he apparently did not observe this property in any of these alloys. G. Masing and O. Dahl⁴ later carried out a systematic study of the hardening phenomenon in these alloys by making hardness measurements as the chief criterion for hardening. When the alloys could be rolled, they were rolled into sheets 1 mm thick or poured into ingots to form plates from 5 to 7 mm. thick. The pieces were quenched from 800°C, heated for one hour at temperatures ranging from 200 to 450°C, and their Brinell hardness was measured, using a ball of 2.5 mm. diameter with a load of 62.5 or 187.5 kg.

With beryllium contents of less than 1.32 wt.% the aging had no effect on hardness; with higher Be contents it changed a great deal and reached the value of 500 kg./mm.² A comparison with the constitutional diagram shows that with the drawing temperatures used and with beryllium contents of 0.75 wt.% upward we are in the region of the super-saturated α solid solution obtained by quenching. The result was unexpected. The experiment was continued. They prepared alloys ranging from 0.77 wt.% Be to 5 wt.% Be. With the alloy containing 0.77 wt.% Be, at none of the temperatures investigated in the range of 200° to 400°C, did any changes in the hardness occur which exceeded the limits of error.

With a Be content of 1.26 wt.% and at temperatures of 200° and 250°C no aging took place. The same alloy at temperatures of 350° and 400°C showed some increase in the hardness after 4 hours of aging and then the hardness decreased as the aging time increased. At all of the temperatures observed between 200° and 400°C this alloy is in the region of super-saturation.

Fig. 2. Comparison of the hardness of the Cu-Be alloys.

Fig. 2. Comparison of the hardness of the Cu-Be alloys.

In spite of the fact that the super-saturation is certainly greater at the lower temperatures than at the higher, the sluggishness of the reaction in the former case is still too great to produce changes in the hardness.

With a Be content of 1.32 wt.%, increases in the hardness took place to a greater degree, but still did not reach the values obtained with higher Be contents. Masing and Dahl⁵ described this characteristic phenomenon in terms of the so-called "induction periods" known from the investigations carried out by Wilm, Fraenkel and Seng⁶ on duralumin. In the latter alloys it is suggested that the age-hardening does not start immediately with the heat treatment, but only after an incubation time has elapsed.

With a Be content of 1.82 wt.%, the increase in the hardness took place to the fullest extent even though more slowly than in the presence of the higher Be concentrations. Furthermore an induction period was observed here even though weaker than in the series of experiments previously described. The induction period for alloys containing greater than 2.4 wt.% Be was too short to measure.

Masing and Dahl continued their experiment by cold working the specimen after quenching but before aging. The cold work did not change the aging behavior of the Cu-Be alloys. They summarized their experiment as follows:

1. The beryllium-copper alloys containing less than 1.5 wt.% Be are not suitable for age-hardening.
2. The Be-Cu alloys containing 1.5 to 4 wt.% Be show a marked degree of age-hardenability after quenching from about 800°C. followed by artificial aging at 250° - 400°C.

3. The hardness of the beryllium-copper alloys increases to about 400 Brinell units.

4. Cold working after the quenching, but before the artificial aging, does not have any noteworthy effect on the age-hardening.

5. The hardness of Cu-Be alloys remains practically unchanged after being heated 107 days at 250°C . When heated to higher temperatures the hardness decreases.

These are very important results, and in the coming pages the characteristics of the Cu-Be system will be further probed by using the nuclear magnetic resonance techniques generally, and the nuclear quadrupole interactions between the copper nuclei and their environment, in particular. Before doing that, however, the changes in the electrical conductivity of the Cu-Be alloys during aging, and various aspects of the nuclear resonance theory will be discussed.

1.2 Changes in the Electrical Conductivity and Other Possible Methods of Monitoring the Precipitation Process in the Cu-Be System

The pronounced age-hardening effect which has been observed in the copper-beryllium alloys has made it seem desirable to study the changes in the other physical properties, so that the nature and cause of the age-hardening mechanism might be understood. In this connection, the investigation of the electrical conductivity might be considered a possible, and important tool.

According to the investigations by Fränkel and Scheuer⁷ it is known that when duralumin is age-hardened at the usual temperature, the electrical conductivity drops about 7%. If duralumin is age-hardened at higher temperatures, the conductivity first decreases and then increases. In view of the age-hardenability of the Cu-Be alloys a change in the electrical conductivity was also to be expected.

In the Cu-Be alloys a relation similar to that in the case of duralumin is found.⁸ While age hardening which is begun by heating at higher temperatures is accompanied by an increase in electrical conductivity, at a lower temperature it is accompanied by a decrease in the conductivity.

When the artificial aging is done at 200°C, the conductivity first drops to about 10% of its initial value for all the compositions. However, after a certain annealing period, the conductivity changes and begins to rise. With the alloy containing 2 wt.% Be aged at 200°C it takes 20 hours before the conductivity begins to increase, with the 2.5 wt.% alloy it takes 7 hours and with the 3 wt.% alloy only 3 hours. The hardness values show no change in direction corresponding to this reversal in the conductivity curve.

At an aging temperature of 250°C the action is accelerated. In the case of the 1.5 wt.% alloy the conductivity first drops slightly, reaching its minimum value after about 16 hours, after which it begins to rise slowly. During this time the hardness is scarcely changed. The 2 wt.% alloy at 250°C shows a drop in conductivity for a period of 4 hours. From this time on it rises quickly. The hardness increases rapidly from the beginning. With the 2.5 wt.% Be alloy the conductivity reaches its lowest value after a half hour.

Also at the aging temperature of 350°C in the case of 1.5 wt.% Be alloy the picture does not change to any great extent, the conductivity decreases more rapidly at first. With the 2% alloy the conductivity first drops and then rises rapidly after a period of 1/2 hour. At this point the hardness shows a distinct induction period. The 3% alloy shows no drop at all.

This action is accelerated still more at a temperature of 450°C . The 1.5 wt.% Be alloy shows scarcely any drop in electrical conductivity, which rises quite rapidly after a short period of time. With the 2% alloy the conductivity drops at the beginning and afterwards rises very rapidly. The hardness shows a corresponding induction period. With the 2.5% and 3% alloys the changes in the electrical conductivity and hardness take place very rapidly. A drop in the conductivity is no longer observed.

The details of the age-hardening action, in general, appear to be dependent upon small changes in the structural characteristics of the precipitating phase and its relation to the matrix. A drop in the electrical conductivity is a phenomenon accompanying the age-hardening which occurs at certain temperatures. On the other hand, the hardness displays an induction period, a delay in initial hardness change. Since the change, as such, is retarded, the same might be expected to apply to the change in conductivity. A plausible explanation of these effects is that coherent β' nuclei, responsible for the initial conductivity change, have no effect on the hardness.

The general observation has been that in the Cu-Be alloys aging at the temperatures of 200°C and below causes a decrease in conductivity, while aging at temperatures of 450°C and above causes an increase in the electrical conductivity. There is an intermediate temperature range in which the conductivity first decreases and then increases.

It is generally agreed that the nucleation and growth of the coherent β' particles set up substantial strains in the matrix. Since these change the electric field gradients at the sites of the copper nuclei (which, otherwise, would have been in an electric field of cubic symmetry) the nuclear quadrupole

interactions could be employed to investigate the aging mechanism in this system with its accompanying hardness and electrical conductivity trends. X-ray analysis is another powerful tool. In fact, Else Holm, Otto Dahl and George Masing⁹ carried out an extensive study of the age-hardening process in the Cu-Be systems verifying, in effect, the initial coherent nature of the β' -crystals. Their observations are summarized as follows.

1. The β' crystals have CsCl structure corresponding to the compound, CuBe, the lattice constant being 2.70 kX.
2. During the age-hardening at 350°C. of the supersaturated α -solid solutions containing 2 wt.% and 2.5 wt.% Be, the β' -crystals separate out in a form which can be detected by means of X-rays. Their lines show no indistinctness. The lines of α -crystals become somewhat indistinct in this case.
3. During the age-hardening at 150°C the (331) line of the α -solid solution widens after a period of 4 hours, which fact is indicated by the indistinctness of the K α -doublet. This indistinctness is considered proof of the presence of coherent β' particles. An electrical resistance increase accompanies this change.
4. During longer age-hardening periods at 150°, 200° and 250°C., the lines of the α -crystals become indistinct to such an extent that the widening cannot be due to just the differences in the concentration of the α -crystal which result from the precipitation of the β' -crystals. This indistinctness could have been caused by the appearance of internal strains during the formation of the β' -nuclei.

5. The β' -crystals which are precipitated out during the age-hardening of the cold drawn wires also show a fibrous structure.

These observations further indicate that the nuclear magnetic resonance technique of observing the redistribution of the solute and the strains resulting from the precipitated particles has possibilities of useful application. This will become clearer after the theory of this technique is discussed in the next chapter.

CHAPTER II - THE THEORY OF NUCLEAR MAGNETIC RESONANCE

Before going into the discussion of the practical aspects of the NMR experiments, at least one quantity needs to be considered; it is the electric quadrupole moment of the nucleus. The electric quadrupole moment is defined in terms of the volume integral

$$Q = \frac{1}{e} \int \rho (3z^2 - r^2) dV,$$

where e = electronic charge

ρ = $\rho(x, y, z)$ = charge density

z = z -coordinate

r = radial distance from the center of mass

In polar coordinates

$z = r \cos \theta$, and

$dV = r^2 \sin \theta dr d\theta d\phi$. So,

$$Q = \frac{1}{e} \int_0^\infty \int_0^\pi \int_0^{2\pi} \rho (3r^2 \cos^2 \theta - r^2) r^2 \sin \theta dr d\theta d\phi$$

Now suppose we have spherical symmetry; that is, ρ is a function of r only.

$$\rho = \rho(r)$$

$$Q = \frac{1}{e} \int_0^\infty \int_0^\pi (2\pi) \rho(r) (3r^2 \cos^2 \theta - r^2) r^2 \cos \theta \, dr \, d\theta$$

$$Q = \frac{2\pi}{e} \int_0^\infty \int_0^\pi \rho(r) r^4 (3 \cos^2 \theta - 1) \sin \theta \, dr \, d\theta = 0.$$

Under the conditions of spherical symmetry, $Q = 0$, a non-zero Q corresponds to non-spherically symmetric distribution of charge; i.e.,

$$\rho = \rho(r, \theta, \phi).$$

We could reduce the integral to a summation if we assumed localized charge. We could write

$$Q = \frac{1}{e} \sum_{i=1}^Z e (3z_i^2 - r_i^2),$$

or,

$$Q = \sum_{i=1}^Z (3z_i^2 - r_i^2).$$

For example, let us look at a nucleus with 6 protons, all at a distance of R from the center of the nucleus, and located on the coordinate axes.

What is the quadrupole moment of such a configuration? Carrying out the summation along different axes, we find that for the z -axis particles:

$$r_i = R \text{ for both particles and}$$

$$z_i = \pm R, \text{ so } z_i^2 = R^2.$$

As a result, $3z_i^2 - r_i^2 = 3R^2 - R^2 = 2R^2$. This is the contribution to the sum from each particle on the z -axis. In the case of x -axis particles

$$z_i = 0 \quad \text{and} \quad r_i = R; \text{ so,}$$

$3z_i^2 - r_i^2 = -R^2$, and the same for the y-axis particles.

$$Q = \sum_{i=1}^Z (3z_i^2 - r_i^2) = 0$$

This is an important result. It shows that even in the absence of spherical symmetry Q can be zero. What happens if z-axis particles are pushed in so that they are $1/2 R$ away from the center instead of R ? One would get a negative value for the quadrupole moment, $Q = -3R^2$. So, if Q is negative it indicates a discus shaped nucleus. Similarly, a positive Q indicates an elongated nucleus.

Q for copper is -0.157 barns. Thus a copper nucleus with its flattened shape will respond to the electric field gradients that are produced at its site by the external charge distribution. The EFG represents the magnitude of the second derivative of the electrostatic potential at a nucleus due to all charges outside the nucleus. At any point in a lattice which is the center of cubic symmetry the EFG vanishes. This fact is basic to this entire experiment. With deviation from cubic symmetry at copper sites (brought about by dislocations, foreign atoms, precipitated particles, etc.) the measurable quantity (nuclear absorption) will decrease. A discussion of the resonance conditions and the theory of the experiment will show how this occurs.

In these experiments, one places the nuclear spin system in a magnetic field H_0 , considered to be in the direction of the z-axis of a coordinate system. As mentioned before, the potential energy of the

orientation of a nuclear moment is $E_0 = - \vec{\mu} \cdot \vec{H}_0$. Since m is the z component of I this becomes $E_0 = - \gamma \hbar H_0 m$, where γ is the gyromagnetic ratio. In the presence of the strong external magnetic field, therefore, the nuclei have discrete energies, occupying one of the $2I + 1$ states. The energy separating adjacent levels is $\Delta E = \mu H_0/I$. For Cu, with spin $3/2$, there will be four such levels, for which $\Delta E = \gamma \hbar H_0$. The m values, which are $3/2, 1/2, -1/2, -3/2$, index the levels.

If we somehow cause transition between these energy levels to occur, the radiation involved will have energy ΔE , with a corresponding frequency ν ;

$$\Delta E = h\nu = \gamma \hbar H_0.$$

It follows that

$$\nu = \frac{\gamma}{2\pi} H_0;$$

this frequency is the Larmor precession frequency of the nucleus. It is in the radio frequency range for atomic nuclei in usual laboratory fields (of the order of 10^4 gauss.). For Cu^{63} nuclei, for example, $\nu = 11.285$ Mc/sec. in a field of 10,000 gauss. Stimulated emission and absorption will occur when an additional magnetic field H_1 , orthogonal to H_0 , is present, if H_1 has frequency ν . This is the phenomenon of nuclear resonance.

Next we have to consider the probabilities involved in occupying the different nuclear energy levels. According to the theory of the Einstein coefficients, the probability of a transition upward to the next higher energy level by absorption of radiation from the field is equal to the probability of transition downward by stimulated emission of rf energy. If all levels were equally populated, there would be no net absorption or emission of energy.

Rowland has discussed the conditions under which the populations are not equal.¹⁰ One turns on the static field H_0 (to cause the splitting). After a time longer than T_1 (T_1 is the spin-lattice relaxation time) the nuclear spin system will be in equilibrium with the heat reservoir (the lattice). Defining P_m as the relative population of the m^{th} level, the level populations are related by the Boltzman factor

$$\frac{P_m}{P_{m-1}} = \exp \left[\gamma \hbar H_0 / kT \right],$$

where k is the Boltzman constant, and T is the lattice temperature. At the normal rf field levels, there are more nuclei at lower energy levels. Since the transition probabilities are the same, there will be a net absorption of energy from the rf field by the nuclei, the absorption occurring in a narrow region in the vicinity of the frequency ν . In general, however, a nucleus encounters not only the external field, but the field set up by other neighboring nuclei as well. This gives rise to a shape function, $g(H)$, which describes the variation in susceptibility with the external field at constant frequency ν ; $g(H)$ has approximately a Gaussian or Lorentzian shape.¹¹

In addition to the usual inhomogeneities in the laboratory magnetic field, there are other more important physical causes for the shape of $g(H)$. There will be nuclear spin-lattice interactions, there are spin-spin or dipolar broadening effects (mentioned above), and there are perturbations due to deviations from the cubic symmetry of the lattice brought about by imperfections.

The measured line width for Cu^{63} is 6.6 gauss. In the following discussion this line width is taken to be the distance between the maximum and minimum slope of the absorption signal whose shape is described by $g(H)$. As will be shown later, the measuring process automatically records the derivative of $g(H)$, facilitating the line width measurements of this type.

The intensity of the absorbed energy is proportional to the area under the curve,

$$I \propto \int_0^{\infty} g(H) dH,$$

However, if the line width remains constant in a series of experiments, the recorded amplitude can be directly utilized as a measure of intensity, for comparison purposes. The amplitude of a reference signal can be used as a normalization factor to correct for the day-to-day drifts in the electronic apparatus, and other experimental parameters over which we have no control. In the case of pure Cu, the electric field gradient at the nuclear sites vanishes because of the cubic symmetry of the lattice; as a result, all the nuclei resonate at very nearly the external field H_0 , and a maximum amplitude is obtained. Once deviations from cubic symmetry are introduced, the EFG at nuclear sites will not be zero. The resultant shift of the nuclear energy levels causes many nuclei not to contribute to the measured amplitude around H_0 , thus reducing the observed intensity. A rigorous derivation of the splitting from such gradients has been formulated,¹² according to which the energy separating the levels m and $m-1$ is given by

$$E'_{m \rightarrow m-1} = \Delta E + (2m-1) (3 \cos^2 \theta - 1) \frac{3e^2 q Q}{8I(2I-1)},$$

where ΔE is the energy level separation in the absence of any quadrupole effects, and θ is the angle between the magnetic field, H_0 , and the axis of symmetry of the EFG. Other symbols retain their previous meanings. Thus the energy separating two levels is dependent on the levels which are considered. Calculations also show that the contribution of the various level transitions to the total intensity is not the same for all transitions but is proportional to $I(I+1) - m(m-1)$ ¹³ for the transition $m \rightarrow m-1$. Thus for the case of pure Cu, 30% of the signal comes from the $3/2 \rightarrow 1/2$ transition, 40% from the $1/2 \rightarrow -1/2$, and 30% from the $-1/2 \rightarrow -3/2$ transitions. The $1/2 \rightarrow -1/2$ transition is called the central transition, while the others are called satellites. A minute amount of impurity may reduce the signal intensity to 0.4 of that of the pure Cu. This is a fact that has been utilized throughout the experiment.

CHAPTER III - EXPERIMENTAL PROCEDURE

3.1 Preparation of Samples

A total number of nine different samples were used in this experiment, eight of which were cast in the laboratory; the last one was a commercial alloy. Following is a list of these samples:

Sample No. 1	Pure Cu
Sample No. 2	Cu - 0.36 at.% Be (0.05 wt.% Be)
Sample No. 3	Cu - 1.00 " " (0.143 " ")
Sample No. 4	Cu - 3.49 " " (0.509 " ")
Sample No. 5	Cu - 6.93 " " (1.045 " ")
Sample No. 6	Cu - 9.87 " " (1.530 " ")
Sample No. 7	Cu -12.54 " " (2.000 " ")
Sample No. 8	Cu -11.12 at.% Be - 0.94 at.% Co (1.74 wt.% Be - 0.98 wt.% Co)
Sample No. 9 (Berylco 25)	Cu -11.32 at.% Be - 0.147 at.% Co (1.76 wt.% Be - 0.150 wt.% Co)

For the laboratory cast samples 99.999 + % pure copper was used as the base metal. The purity of the beryllium used was 99.95%. Copper rods weighing about 25 grams were cut from the stock. The rods were cleaned in dilute HNO_3 , and weighed on a Mettler Gram-atic balance. They were then placed in quartz tubes. Proper amounts of beryllium were also weighed and added to the tube contents.

In the case of sample No. 8 a cobalt-rich alloy of copper-beryllium (Beryco 10: 0.40 - 0.70 wt.% Be, 2.35 - 2.70 wt.% Co. and balance Cu) was used in proper amount as a Co source.

After all the charges had been placed in quartz tubes of the same diameter, the tubes were necked in a high intensity torch flame for ease of sealing after evacuation. The tubes were evacuated in a pressure of less

than 0.2 microns after the entire vacuum system had been flushed several times with pure argon. The tubes were also heated slightly after the low pressure had been achieved, in order to get rid of the possible adsorbed moisture. Then the tubes were sealed.

The samples were melted in a resistance furnace held at a temperature about 30°C . above the melting point of beryllium. The samples were held in the molten state for 15 minutes; then they were vigorously shaken and left in the furnace for 5 more minutes. Subsequently, the molten alloys were quenched in water having a temperature of 15°C . The surface of the castings was generally clean, and the quartz tubes did not break upon quenching. The samples were then filed in a filing machine which essentially simulated the hand filing operation. The size of the powder finally separated out and used was less than 200 mesh ($\leq 74 \mu$). The weight of all the powder samples was 2.256 grams. Each powder sample was mixed with a known amount of vanadium powder, and then the total volume of the samples was raised to 1.7 cc by adding alumina powder. Vanadium was used as a standard, and the purpose of alumina was to prevent sintering of the sample powder during high temperature solution heat treatments.

Each sample was first tested in the as-filed condition in a quartz tube. Then the tubes were evacuated as before and sealed. The seal was never broken in the course of the experiment. The samples were solution heat treated at 800°C . for 24 hours. They were quenched and tested. Then they were aged at different temperatures (depending on their concentrations of Be). Each sample at a constant temperature was aged for different periods of time and tested after each aging treatment. The aging temperature used for each sample is given in the following table:

Sample No. 2	Cu - 0.36 at. % Be	230°C
" " 3	Cu - 1.00 at. % Be	200°C
" " 4	Cu - 3.49 at. % Be	250°C
" " 5	Cu - 6.93 at. % Be	320°C
" " 6	Cu - 9.87 at. % Be	320°C
" " 7	Cu - 12.54 at. % Be	320°C and 450°C
" " 8	Cu - 11.12 at. % Be	320°C and 430°C
	0.94 at. % Co	
" " 9	Cu - 11.32 at. % Be	430°C and 450°C
	0.147 at. % Co	

The amount of vanadium that was mixed with each sample is shown below:

Sample No. 1	mixed with	0.320 gm Vanadium
" " 2	" "	0.320 gm "
" " 3	" "	0.107 gm "
" " 4	" "	0.148 gm "
" " 5	" "	0.147 gm "
" " 6	" "	0.089 gm "
" " 7	" "	0.035 gm "
" " 8	" "	0.236 gm "
" " 9	" "	0.049 gm "

In the section on experimental data in the next chapter a thorough discussion of the use of these values in making intensity measurements has been given.

Sample No. 9 which was the commercial Berylco-25 alloy was obtained in the form of a rod. This alloy is a wrought material and responds to aging very readily. Its composition was determined by chemical analysis.

3.2 Description of Electronic Apparatus

The electronic apparatus employed in this experiment is capable of measuring the relative values of the absorbed energy at the resonance frequency of the matrix nuclei, thus yielding a qualitative, or semi-quantitative, measure of the magnitude of the EFG at the nuclear sites. Solute atoms, second phase particles, or dislocations may cause the EFG.

The external magnetic field, H_0 , is produced by a Pacific Electric Motor Company electromagnet and power supply. The latter provides a stable d.c. current by means of its transistor regulated silicon rectifier unit. A motor driven potentiometer in the control circuit varies the field linearly with time over a region including the resonance.

A standard model V-4210-A Varian variable frequency transmitter-receiver unit provides the rf field, signal amplification, and detection. The Varian probe used contained the crossed coils, the balancing paddles, and the coils for modulation. A Hewlett-Packard model 200 ABR audio oscillator driving a Dynakit Mark III 60 watt audio power amplifier supplied power to the coils on the probe body for field modulation. From 0.2 gauss to 90 gauss 20 Hz sinusoidal modulation was available for use. A lock-in amplifier (phase sensitive detector) was used for narrow banding the system to about 0.01 to 1 Hz, using filtering of the synchronous detector output. An L & N speedomax G pen recorder recorded the lock-in output. A block diagram of all these components appears in Figure 2. The speed of the recording chart was 15 inches per hour. The field scanning unit was driven by a synchronous motor. The chart was calibrated in gauss/inch by centering a signal on the scope, rotating the scanning dial 10 revolutions and re-centering the signal by changing the frequency. From the frequency change involved

it was found that every 13.36 inches of the chart corresponded to 117.9 gauss at a field strength H_0 near 10,000 gauss. The absorption mode of the resonance signal was recorded at room temperature at a frequency of 11.326 Mc/sec. with an external field of about 10,000 gauss. The modulation amplitude was set at 3.0 G peak to peak and H_1 was about 0.05 oersted.

The reference vanadium signal and the Cu^{63} signal were recorded in each case in a single run of about one hour. The resonance fields of V^{51} and Cu^{63} are very close.

Figure 2 The block diagram of the electronic apparatus.

CHAPTER IV - EXPERIMENTAL RESULTS, DISCUSSION AND CONCLUSIONS

4.1 Experimental Data

As mentioned in the last chapter, the metal vanadium was used in this experiment as a reference standard. Another possible technique to use in standardizing the copper signals from different samples would be to break the sample container after each heat treatment and to use a vial containing pure aluminum or vanadium powder, trying each time to place it exactly at the same location in the sample tube. (The resonance frequency of Al^{27} is also very close to that of copper, although not as close as the resonance frequency of V^{51} .) The act of breaking the seal so frequently and transferring the specimen to a new tube for re-evacuation and re-heat treatment could cause some uncertainties in the measurements. The use of vanadium powder mixed with the specimen powder for standardization made it possible to keep the specimen tubes sealed throughout the experiment. In addition a random mixture of the vanadium and the specimen powder was ensured by shaking the tubes before testing.

Vanadium powder was chosen as a standard because of its (a) very high melting point, (b) high degree of stability at elevated temperatures, (c) conveniently close resonance frequency to that of Cu^{63} , and finally (d) high isotopic abundance and strong signal intensity.

The experiment with this new method of standardization was very successful in many respects. In the early phases of the work, copper beryllium alloys of different concentrations and the commercial alloy were tested. The vanadium signal amplitude in each case was used as a normalizing factor for Cu^{63} signal amplitudes.

The solution heat treatment temperature for all the alloys was 800°C . The same temperature was used in the annealing of pure Cu (mixed with vanadium and alumina). Pure Cu was also tested after annealing at 800°C mixed with alumina alone, using a vial of aluminum powder for standardization. In both cases the Cu^{63} absorption amplitude of the annealed sample was about 15% greater than that of the as-filed sample. When an annealing temperature of 500°C was used, the rise in the signal amplitude of Cu in the annealed condition, as compared to the as-filed condition, was about 50%. Apparently, some impurities are introduced into the copper at 800°C . An experiment with vanadium alone mixed with alumina, heated at 800°C for 24 hours, showed that vanadium intensity decreased about 8% after the treatment, but this is within the experimental error.

The conclusion is that the temperature of 800°C is too high for annealing pure copper, mixed with alumina.

All the alloys were tested in the as-filed, solution treated, and aged conditions. The aging times were 15 min., 1/2 hour, 1 hr, etc. The signal intensity of a sample of pure Cu annealed at 800°C was set arbitrarily at unity, and other signal intensities were normalized to this value.

There are essentially three sets of data.

Set 1. compares the signal intensities of all the alloys, as well as the intensity of pure Cu in the solution heat treated (annealed) state. These data show what fraction of the Cu^{63} nuclei contribute to the resonance intensity in the presence of a certain concentration of the solute atoms randomly positioned on the lattice.

Set 2. compares the intensities of the Cu^{63} signal in all the alloys in the as-filed condition (cold worked) with the intensities in the annealed

(solution heat treated) condition. This gives an indication of the effect of dislocations on the resonance intensity.

Set 3. deals with the aging process. It shows the change of intensity as a function of aging time at various temperatures. These data indicate the influence of the second phase particles on the resonance behavior of the Cu^{63} nuclei in the matrix.

Data corresponding to Set 2. and Set 3. appear on the same graph.

In the case of the Set 1. data, normalized intensities have been plotted as a function of $\ln(1-c)$, where c is the atomic percent of solute. The rationale behind this is that any copper atom which has no solute on the n sites within a critical radius R_c will contribute its full share to the observed intensity.¹⁴ If the atomic percent of the solute in the alloy is c , then each lattice site has a probability of $(1-c)$ of being occupied by a copper atom. For n sites this probability is $(1-c)^n$. This is, in turn, a measure of the observed intensity, or equivalently, the observed amplitude (as long as the line width and shape do not change very much). So the log of the normalized amplitude as a function of log of $(1-c)$ should be a straight line with the slope, n . These data are shown in Figure 3. The data corresponding to Set 2. and Set 3. appear in Figure 4. The data related to the aging behavior of the commercial Berylco-25 and the tensile strength data of the same alloy are shown in Figure 5. The laboratory-cast alloy of high Co content (Sample 8) did not respond to aging (probably due to the lack of the dissolution of beryllites in the Berylco-10 alloy, which was used as the cobalt source). The high temperature and low temperature aging behavior of the Cu - 2 wt.% Be alloy (Sample 7) is presented in Figure 6. Sample 8 may have had much less free Be than sample 7 because of the formation of Co-Be compounds (beryllites).

Figure 3 Intensities of solid solutions of copper-beryllium.

Figure 4 Effect of dislocations and the second phase particles on the Cu^{63} resonance intensity.

Figure 5 The aging behavior of Berylco-25 and its relationship to the tensile strength.¹⁵

Figure 6 Resonance intensity of Cu^{63} in Cu-2 wt.% Be alloy aged at two different temperatures.

4.2 Discussion and Comparison with Some of the Other Alloys

By using a combination of the phase diagram and Figure 3, let us calculate the intensity of the Cu^{63} resonance in the Cu - 12.54 at.% Be alloy (alloy No. 7) after it has been aged at 320°C ; and then let us compare the result with the intensity of the same sample in the solution treated state. Similar calculations may be carried out for the other alloys.

According to the Lever Rule, the Cu - 2 wt.% Be supersaturated solid solution decomposes into two phases, α and β' , with 81% being α and 19% being β' . Neglecting the contribution, if any, to the resonance intensity of the Cu^{63} nuclei in the β' phase, one may calculate the resonance intensity of the central line of Cu^{63} in the α phase which has a composition of about 2 at.% Be.

$$\ln(1 - c) = \ln(1 - 0.02) = \ln 0.98 = -0.022.$$

From Figure 3, the corresponding normalized amplitude is 0.65. But this would be the amplitude if we had 100% α . With 81% of the total matter being α , the calculated intensity will be 0.52. The observed normalized amplitude of this alloy after 8 hours of aging at 320°C is 0.2, from Figure 6.

If we repeat these calculations for the same concentration alloy at an aging temperature of 450°C , we obtain a calculated amplitude of 0.32, as compared to its experimental value, which is 0.22 (Figure 6). The same alloy in the solution treated state has a normalized amplitude of 0.072, used in the determination of n from Figure 3.

In view of the long aging times and high temperatures used in these cases, and in view of the aging behavior of this alloy, described in Chapter I, precipitation does take place in this alloy, and still its observed resonance intensity is below the expected value. It is possible that the precipitated

particles remain coherent with the matrix and set up internal strains which do not allow full rise in the resonance intensity. These internal strains have been the subject of X-ray studies¹⁶ and have been shown to exist. For example in the observations of E. Holm, O. Dahl and G. Masing, cited in Chapter I, we found that at an aging temperature of 350°C, the diffraction lines of the α -phase of the 2 wt.% Be alloy became indistinct upon aging. The conductivity in this case begins to rise after less than 1/2 hour of aging and shows no subsequent drop.

Aging in copper-beryllium alloys is known to be an inhomogeneous process; precipitation takes place preferentially at the grain boundaries. (This was pointed out to us by Professor Paul A. Beck.) A consequence of this inhomogeneous aging process could be depletion of the matrix which would promote the presence of coherent β' particles inside the grains.

To sum up, in the case of the 2 wt.% alloy both the conductivity and the resonance absorption intensity have begun to rise after a short period of aging at 320°C. The initial rate of rise is faster for the case of aging at 450°C. A similar agreement is observed in the case of other alloys, with lower Be concentrations and lower aging temperatures, where there is no noticeable rise in their resonance absorption intensity and, similarly, there is a long initial period where their conductivity continues to decrease. These alloys further have the property that their hardness shows a very long induction period during aging at the temperatures that have been used. The observations made on the resonance intensity, conductivity and hardness appear to be in reasonably good agreement.

In considering the differences between the resonance amplitude of alloys in the as-filed and annealed conditions, one inevitably has to study the effect of dislocations.

The imperfections in a crystal which will cause a perturbation of the nuclear energy levels may be classified into four categories, namely, impurity atoms, vacancies, dislocations and stacking faults. The nuclei interact with the electric field gradients produced by them. However, the effects due to vacancies, interstitials and planar defects at room temperature are either non-existent or minimal. Manintveld,¹⁷ and Lomer,¹⁸ and Votava¹⁹ have studied the effects of point defects, interstitials, and planar defects, respectively. The vacancies in copper migrate at temperatures below room temperature. They move to the dislocations or to the surface where they cannot affect the experiment. Interstitial Cu atoms have a relatively high energy of formation (4.0 ± 1 eV.) and probably are not produced by filing.

Votava did not observe stacking faults in the electron transmission microscopy of cold worked copper.

As far as the electric field gradients produced by dislocations are concerned, we will compare the resonance absorption intensity of the copper in the as-filed condition with the intensity of copper after annealing at 500°C for 24 hours. As stated previously, pure Cu was also annealed at 800°C. On an arbitrary scale, the intensity of copper in the as-filed condition was 0.76, as compared to 0.89 for the case of annealing at 800°C and 1.31 for the copper annealed at 500°C. It is seen that annealing at 500°C increased the absorbed intensity by 58% when compared to the intensity in the as-filed condition. Rowland and Bloembergen²⁰ had observed the first order reductions in signal to be 50-60% due to filing.

The intensity of the alloys in the as-filed condition did not appreciably change upon solution treatment. In the case of high Be concentration alloys there was a slight decrease in the resonance intensity. This is possible due to the localized heating produced by the filing operation.

4.3 Conclusions and Summary

The resonance absorption intensity of copper-beryllium alloys has been measured for alloys in the solution treated condition, and it was found that the intensity is proportional to $(1 - c)^{20}$ where c is the atomic percent of Be.

The aging behavior of the copper-beryllium alloys was studied; the results mainly support the previous observations that alloys containing less than 1.5 wt.% beryllium are not suitable for age-hardening and that the addition of Co to the age-hardenable binaries of copper and beryllium hastens the aging process.

The nuclear magnetic resonance intensity measurements of the aged alloys indicated that possibly lattice strains produced by the coherent β' particles are responsible for the intensity attaining only part of its theoretical value.

The absorption intensity of the 2 wt.% Be alloy reached its peak after one hour of aging at 450°C , and then it remained essentially unchanged. Thus, to follow the aging process in the high Be alloys, it is more convenient to use lower aging temperatures.

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