Also the fact that the oscillation frequencies of mesons and baryons are scaled off by $1/\alpha$ and $1/\alpha^{3/2}$ respectively, suggests that the strength of the binding interactions for these particles is of this order. In this context, it may be noted that the strength of the interaction between two Dirac[4,5] monopoles is roughly of this order, *i.e.*, $1/\alpha \sim 137$.

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A STUDY OF METASTABLE EQUILIBRIUM IN ALUMINIUM-COPPER ALLOYS

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ABSTRACT

Hardness and electrical resistivity measurements are carried out on Al–0·75 and 1·50 at·% Cu alloys to study the reversion phenomenon. Critical reversion temperatures for these alloys are found to be in good agreement with the findings of earlier work. The metastable solvus curves for both G-P. zones and θ' phase are thus confirmed with minor modifications.

INTRODUCTION

IN recent times the search for stronger metallic materials has aroused more interest in metastable equilibrium in alloys. By resorting to suitable thermal treatments it is today possible to convert the so-called equilibrium alloys into different non-equilibrium states associated with superior mechanical properties. Apart from its practical aspects, metastability in alloys constitutes a fascinating area for theoretical studies. Among alloys systems explored from the point of view of metastable equilibrium, those based on aluminium occupy a very special place because of their great commercial importance, as also their pronounced age-hardening potential.

Ever since the discovery of the age-hardening phenomenon by Wilm[1] in aluminium-copper (Al-Cu) alloys, this binary alloy system has attracted considerable attention in the metallurgical world. The sub-microscopic structural changes on ageing dilute alloys of this system have been investigated by many workers[2]. The pioneering work of Guinier[3] and Preston[4] led to the identification of the complex sequence of precipitation on ageing in this system as:

Guinier-Preston (G.P.) Zones $\rightarrow \theta'' \rightarrow \theta' \rightarrow \theta$ ($CuAl_2$).

Two peaks are generally observed in the ageing curves of these alloys. It has been shown[5] that the G.P. Zones are responsible for the initial rise in hardness while θ'' and θ' metastable phases give rise to the second hardness peak. Thus the metastable equilibrium on ageing is quite complex in this system.

The metastable solvus for Al-Cu alloys was studied for the first time by Beton and Rollason[6] through a study of the changes in hardness on reversion of the aged alloys. Later, Borelius and Larsson[7] established the metastable phase boundary for G.P. Zones through calorimetry in support of their earlier study[8]. Around this period Gerold and his coworkers[9-11] established and demonstrated the usefulness of the metastable miscibility gaps in aluminium-silver and aluminium-zinc systems. There have, however, been no attempts so far to confirm the earlier work on metastability in Al-Cu alloys although many techniques like tensile testing, calorimetry, resistometry, X-ray small angle scattering and others are today available for the study of the metastable solvus in alloy systems.

The present investigation was undertaken primarily to verify earlier results and incidentally to arrive at a better understanding of metastable equilibrium in the Al-Cu system. Two compositions were selected, one in the lower and the other in the higher concentration range for age-hardenable alloys. Hardness measurement was first used in an analogous way to that of Beton and Rollason[6] to verify earlier results. Later, electrical resistivity measurements were made use of for the first time

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in this system to establish the metastable solvus lines with certainty.

Experimental Procedure

Preparation of Alloys.—Two alloys having compositions Al–0·75 (Alloy I) and 1·50 (Alloy II) at.% Cu were prepared from superpurity aluminium [99·999 + %] and superpurity copper [99·999 + %] using a graphite crucible. After homogenizing for 15–20 minutes the alloys were poured from 700° C into a cylindrical graphite mould of inside diameter 2 cm and length 10 cm. The cast alloys were then homogenized at 400° C for 24 hours and hot forged to plates of 4 mm thickness. Intermediate annealing treatments were given in between the forging operations.

Hardness samples of 3 × 2 cm size were cut from the final plates of 3·2 mm thickness. They were annealed at 400° C for 3 days to ensure complete relief from forging stresses.

The forged plates were rolled into rods with intermediate annealing at 300° C. These rods were then drawn into wires of 0·7 mm diameter. The wire samples were used for the electrical resistivity measurements after annealing for 24 hours at 300° C.

Heat Treatment and Hardness Measurement.—To measure hardness, the massive samples of the alloys were first solution heat treated at 500° C in an electrically heated muffle furnace controlled to ± 2° C. They were then quenched in water kept at room temperature (30° C). From a knowledge of room temperature ageing characteristics of these alloys, they were aged for 24 hours before reheating for various times upto 1 hour in different oil/salt baths maintained in the temperature range of 60° to 240° C, generally at intervals of 10° C. After reversion, the samples were quenched in water and then taken to an ice-water mixture (0° C).

The hardness readings were taken at 0° C for all samples making use of a special specimen-mounting arrangement. The hardness values were evaluated from the readings obtained on a Vickers-Armstrong Hardness Tester, using a 5 kg load from the average of at least four impressions on each sample.

Heat Treatment and Resistivity Measurements.—For measuring electrical resistivity lengths of 25 cm wire were cut and welded in each case to two thin long strips of superpurity aluminium on either side. These formed current and voltage leads. The samples were homogenized at 500° C for a few hours before quenching. Homogenization and quenching operations were repeated a number of times in order to stabilize the specimens. Each time the heat treatment given for the samples was as follows : Solution heat treatment for 1 hour at 500° C, water quenching and ageing for 4 hours at room temperature. This time was found to be sufficient for the maximum growth of zones as indicated by a constant resistance. Then, the samples were reheated to the same temperatures as used for hardness measurements and quenched into water. Resistivity measurements were then made at 0° C with an intermediate dip in acetone to remove traces of oil/salt. The usual Kelvin Double Bridge method was used to measure the electrical resistance.

Hardness on Reversion.—The hardness reversion characteristics of the two alloys are shown in Figs. 1 and 2. None of the experimental points

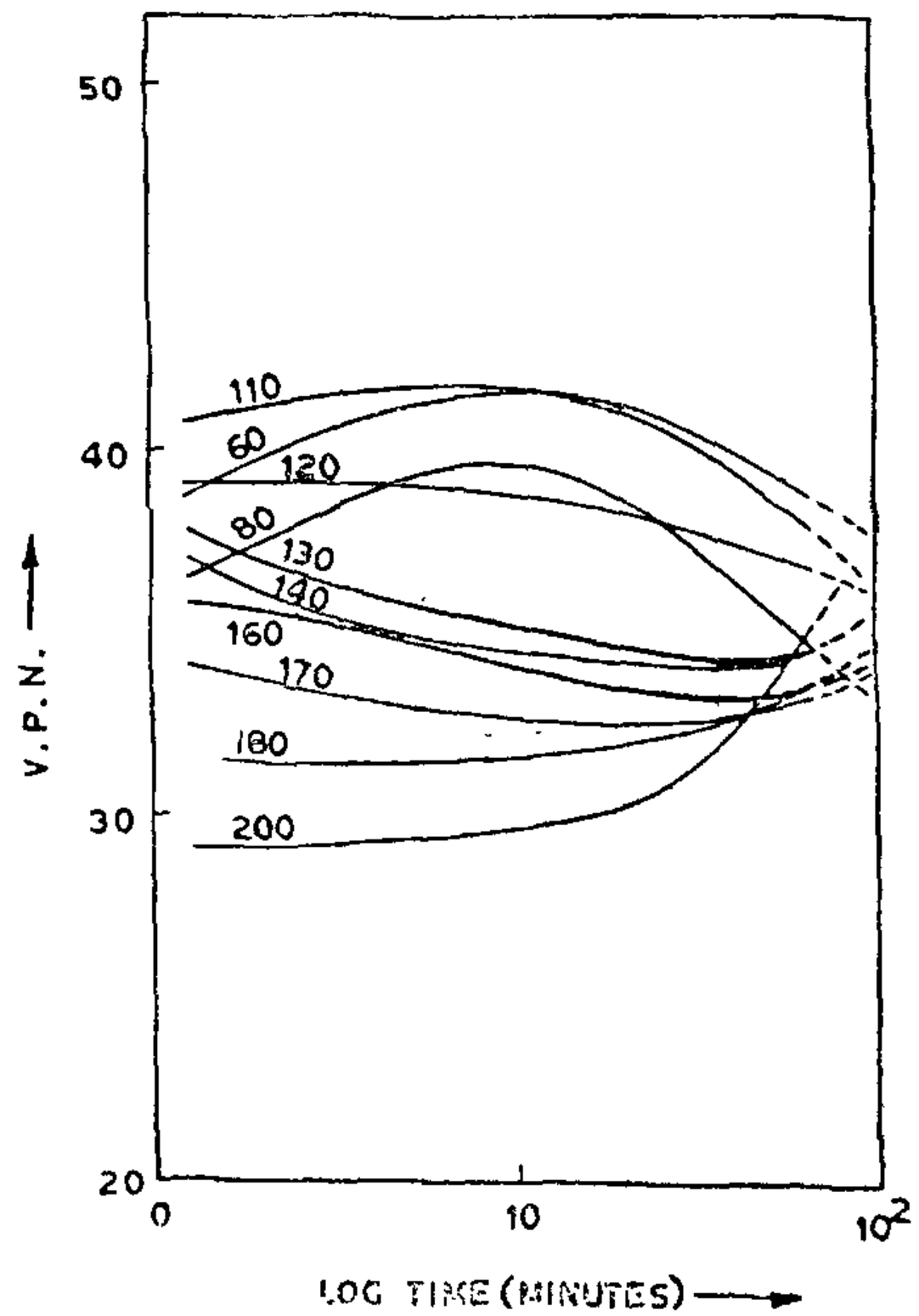

Fig. 1. Hardness *versus* Ageing Time for Different Reversion Temperatures for Al-0·75% Cu Alloy.

are shown for the sake of clarity. The salient features are as follows :

(*i*) A slow increase in hardness to a peak value is observed in the range of 60–110° C for Alloy I while for Alloy II a slightly greater increase is observed in the range of 60–150° C.

(*ii*) From a temperature of 130° to 170° C, in the case of Alloy I, the curves show slow fall in

hardness from the initial value to a constant value, in contrast with the earlier trend. A similar trend is observed for Alloy II in the range 180–200° C with a slower rate in the range of 160–170° C following the peak value.

(*iii*) For temperatures at and above 180° C for Alloy I the hardness increases slowly from the initial value upto about half an hour. Thereafter, a greater increase is observed. On the other hand, for Alloy II a slow increase from the initial value is observed above 210° C for about half an hour. Thereafter the hardness increases rapidly.

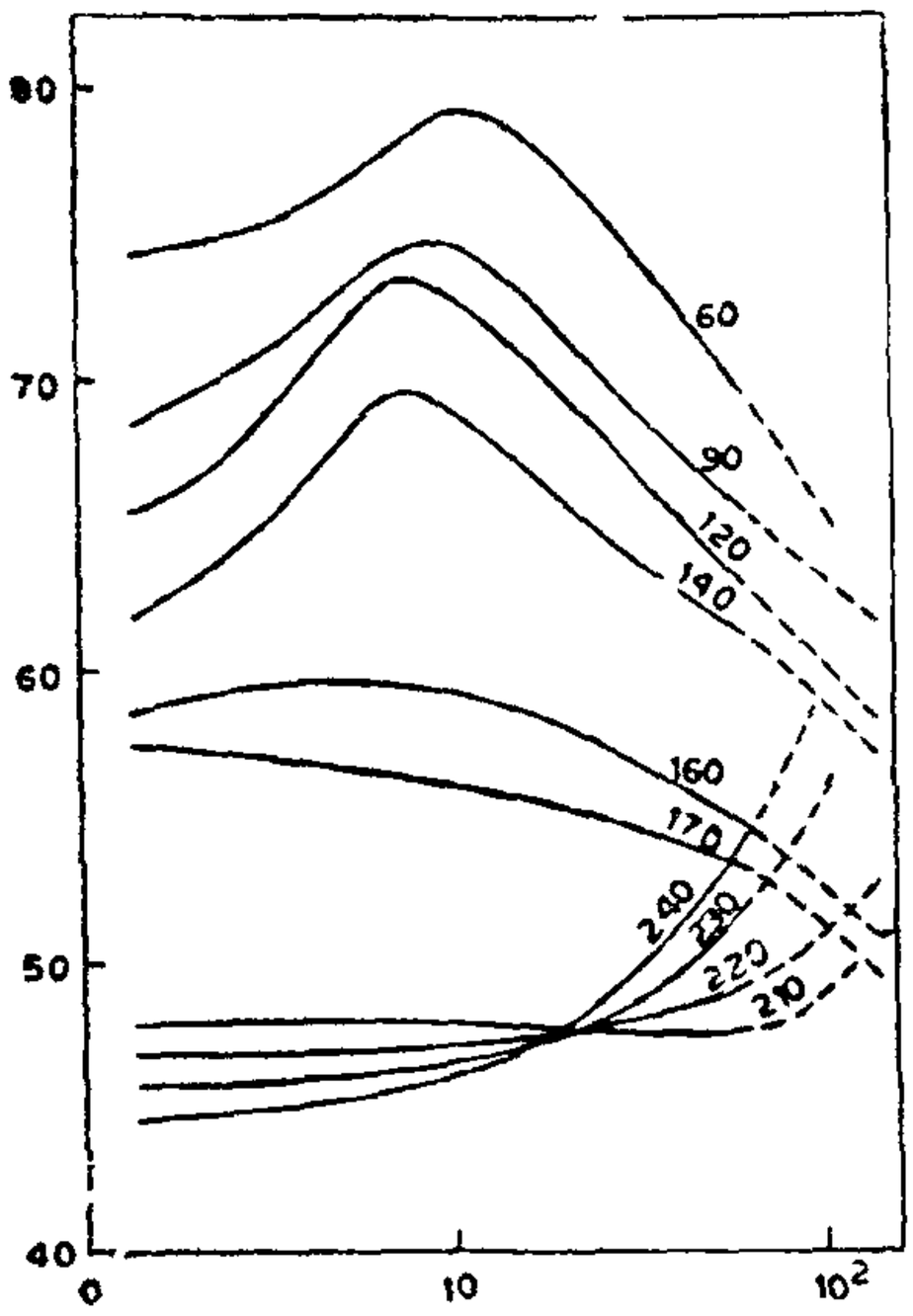

FIG. 2. Hardness *versus* Ageing Time for Different Reversion Temperatures for Al-1·5 at.% Cu Alloy.

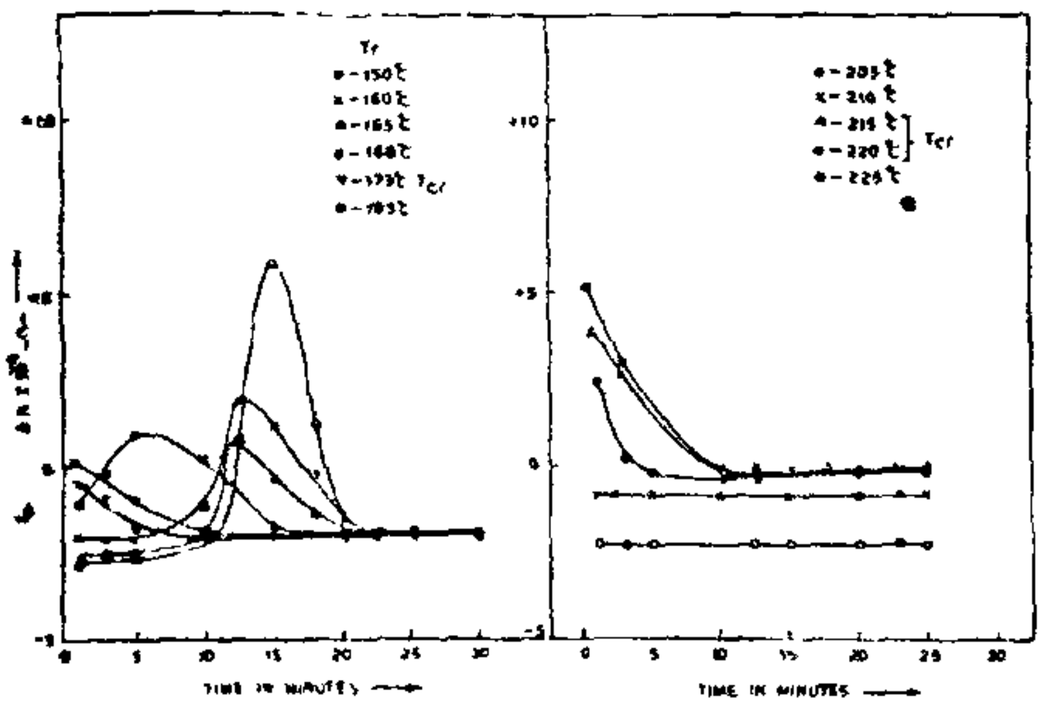

FIG. 3. Electrical Resistance Change *versus* Ageing Time for Al-1·5 at.% Cu Alloy.

Resistivity Data.—Figure 3 shows plots of changes in resistance values *versus* ageing time at all reversion temperatures (T_r) for Alloy II. The change refers to the difference in resistance values obtained at 0° C before and after reverting to various temperatures. The changes in electrical resistance observed in Alloy I are not too marked. Hence the results as well as the discussion have been presented more with reference to Alloy II. However, the same trend is observed in case of Alloy I also except for the fact that in this case the rate is slower because of low concentration of solute. From the figure, the following points are obvious :

(*i*) An initial constant resistance is observed which then reaches a peak followed by a rapid fall upto a temperature of 165° C. However, at 168° C there is no initial constancy in resistance.

(*ii*) For all temperatures upto 185° C, a decrease in resistance is observed resulting in a constant value.

(*iii*) There is more or less constant resistance in the range of 200–210° C.

(*iv*) Above 210° C, a decrease in resistance to a constant value prior to higher initial resistance except at 210° C (which is slightly lower than that at 215° C) is observed. A faster rate of fall of resistance at higher temperatures is obvious.

Discussion

The results described above can be understood in terms of the present-day ideas on ageing and reversion in terms of ageing sequence in Al-Cu alloys. The G.P. Zones formed at room temperature attain same size. After reversion at various temperatures the solute atoms are dispersed as after quenching but with a new rate of formation of zones which is slow due to the rapid annealing out of vacancies at the T_r[12]. Further, at low temperatures, only partial reversion takes place[13]; with a rise in temperature the size of zones increases and they grow with time upto a critical temperature (T_{cr}) at and above which the zones dissolve completely. Below the critical reversion temperature (T_{cr}), the slow decrease in hardness after longer ageing time is due either to the growth of zones above the critical size or the beginning of the dissolution of zones. Thus, the slow increase or constancy in hardness and resistivity can be understood in accordance with the earlier work[14]. However, the rate of increase as well as peak hardness are different in the two alloys because of different vacancy concentrations. The peak indicates the stability of zones. Hence change in peak height and shift to shorter times at higher T_r can be understood in terms of stability and number of

zones at longer ageing times at various temperatures.

Beginning of the total dissolution of zones is indicated by the decrease in the initial value of hardness above 130° C for Alloy I. After complete reversion, hardness and resistance return to constant values. Thus the beginning of decrease in hardness at ~ 130° C and of resistance around 125–130° C indicates these to be the critical reversion temperatures (T_{cr}) for Alloy I. Similarly ~ 170° C (hardness) and between 168–173° C (resistance) are found to be T_{cr} for Alloy II. In this case the initial value of resistance at temperatures above T_{cr} may be due to the attainment of critical size at shorter periods.

Further decrease in hardness and resistance in both alloys are due to large size and small number of zones[14]. However, by this time θ'' starts appearing which is accompanied by an increase in hardness and resistivity. The contribution due to this may be small and hence the effect due to the dissolution of zones may be prominent.

Dissolution of θ'' and formation of θ' results in a decrease of hardness and resistance. It has been established[16] that hardening due to θ'' is greater than that due to θ' and hence even though θ' forms, its influence becomes prominent at longer ageing times only when θ'' completely dissolves. Resistivity due to θ' is smaller than that due to θ''. Also constancy in resistance is expected till the θ' phase is nucleated. Thus, the fall in hardness at 170° C and of resistance between 166–172° C for Alloy I and similar changes at 210–220° C and 215–220° C for Alloy II can be easily understood. Further, the sudden increase in hardness and slow increase in resistance after ageing for half an hour at and above these temperatures may be due to initially nucleated particles of θ' needing a certain amount of time for their growth. If still higher temperatures were used one would expect further fall in resistance till the equilibrium θ phase is precipitated. Thus, the critical reversion temperatures for θ'' are found to be ~ 170° C (hardness) and between 166–172° C (resistance) for Alloy I and 210–220° C (hardness) and between 215–220° C (resistance) for Alloy II.

The Metastable Solvus Curves.—Figure 4 shows the relevant portion of the Al-Cu equilibrium diagram along with the metastable solvus curves for G.P. Zones and θ'' phase. The critical temperatures obtained in the present investigations are included along with those of earlier investigators. The temperatures obtained in the present work are slightly lower than those reported earlier. This may be due to the purity of the metals used and the difference in techniques adopted.

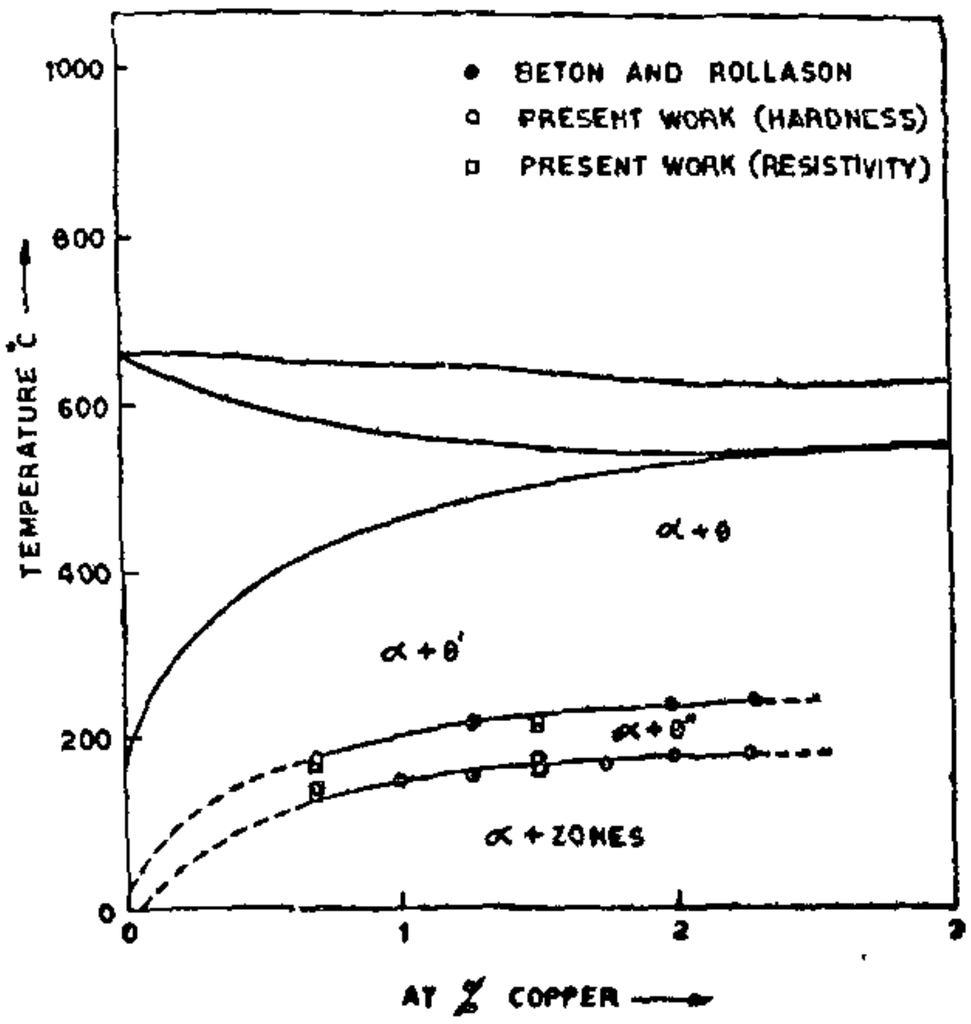

FIG. 4. Metastable Phase Boundaries in Al-Cu Equilibrium Diagram.

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