Research on the Copper-Rich Solid Solution

in Cu-Mn Binary System. I*

Masayuki KAWASAKI, Kenkichi YAMAJI and Osamu IZUMI

The Research Institute for Iron, Steel and Other Metals

Synopsis

The authors investigated the alloys in Cu-Mn system containing manganese up to 61.3 % from various stand points, namely, microstructures, hardness changes due to various heat-treatments, temperature dependence of electric resistivity and thermal expansion, and density at room temperature. The most outstanding results were as follows : (1) The solubility curve of this system was similar to that proposed by Grube with a slight difference in the range of lower concentration, but did not agree with that reported by Ishiwara and Isobe. (2) The alloy with about 10 % of manganese displayed some anomalies in higher temperature range, although it was conceived to be homogeneous solid solution. Furthermore, in the alloys of higher concentration a singular process of a certain transformation type is supposed to have existed, regardless of the solubility change. (3) The activation energy of hardening for the alloy containing 42.9 % of manganese quenched from 750°C and aged at 400°~550°C was about 23,600 cal/mol, but it was very small for the alloy of 61.3 % of manganese.

I. Introduction

Two different types of equilibrium dirgram on Cu-Mn system have been proposed. The one is, according to Ishiwara and Isobe,[1] of the type of a limited solubility with 35.0 % of manganese as the maximum solubility at 850°C, whereas the other, established mostly by E. Persson[2] and G. Grube[3] and others, is of a type of all miscible' solid solution, named γ, whose temperature range becomes narrow with the increase of manganese. Therefore, from the view point of alloy structure at higher temperatures, two distinguished conceptions have been proposed about the alloy containing larger amount of manganese. As stated later, however, the diagram of the latter type also does not seem to be the most satisfactory one becauce of some incompleteness. On the other hand, as already known, either Cu-Mn system or Ag-Mn, etc., possesses the negative temperature coefficient of resistivity in certain compositions, which are well utilized as alloys of standard resistance, such as Manganin, Isabellin etc. It has not yet been clarified as to what kind of mechanism plays the most important role in this phenomenon. In general, these alloys have such a peculiarity that in the temperature dependance of physical properties a fairly strong hysteresis takes place, so that the most stabilized

*   The 621 st report of the Research Institute for Iron, Steel and Other Metals.
(1)   T. Ishiwara, M. Isobe ; Kinzoku no Kenkyu 6 (1928), 381, Sci. Rep. Tôhoku Imp. Univ., 19 (1930), 499.
(2)   E. Persson, Z. Phys. Chem., (B) 9 (1930), 25.
(3)   G. Grube, E. Östreicher u. O, Winkler ; Z. f. Elektrochem., 45 (1939, Oct.,) 776.

change is hardly forthcoming, as has recently been pointed out by O. Heusler.[4] These circumstances, perhaps, make it fairly difficult or confusing to establish more reliable results with respect to the construction of this binary system. From the above considerations, the authors intended to determine first the type of the diagram of Cu-Mn system and then the solubility limit of manganese, especially in the lower temperature range than that known heretofore. If the limit becomes much less than any yet determined at room temperature, it may be possible that the abnormal hardening, found by one of the authors[5] even in the dilute solid solution of this system, would occur easily due to the low-temperature annealing after severe cold-working. On the contrary, when the limit of solubility is not influenced by any treatment, the anomalies observed mainly in the vicinity of 12 % manganese content will, perhaps, be attributable to other causes.

The authors have investigated the problem with the alloys conatining manganese up to about 60 % from various stand points, namely, microstructure and hardness change under various heat-treatments, change of electric resistivity or thermal expansion in heating or cooling process with constant rate, and change of density due to the variation of concentration. In the present report, the experiments on these items are given and in later works researches with regard to röntgenographic structure and specific heats will be given with some theoretical considerations for the anomalies observed hitherto.

II. Experimental Procedures

(1) Samples

The alloys were melted in a high frequency electric furnace and chill-cast into rods 20 mm in diameter and 260 mm in length. After the hot-forging to the diameter of 8 mm, machining, sizing and finishing were successively carried out. Samples for measurements of physical properties were reheated at 750°C for 3 days, followed by extreme slow cooling with the rate of about 50°C per day, in order to obtain the stabilized conditions.

(2) Measurements

Both the total and the differential thermal dilatations were carried out using the dilatometer of Imano's type improved by the authors. For the measurement of electric resistivity, samples were heated or cooled in a partial vacuum with CO_2 current, to avoid the de-manganese effect and oxidation, which could not be prevented by other ways and which would be accompanied with some unfavourable results such as unexpected large hysteresis. To measure the change of resistivity, the potenticmeter was used throughout the tests. Furthermore, the density measurement was done by using an accurate chemical balance by the water-immersion method, taking into account the correction of air buoyancy.

(4) O. Heusler; Z. Metallkunde, 39 (1948) 326.
(5) M. Kawasaki; Rep. of 3 rd section Meeting, Japan Inst. of Met., (Nov. 1949), Unpublished.

III. Experimental Results and Considerations

(1) Solubility curve.

In order to investigate which is the more proper as the solubility curve of copper rich solid solution the type of Ishiwara-Isobe or that of Grube, hardness changes were measured in four alloys containing 23.9 %, 27.2 %, 42.9 % and 61.3 % of manganese, respectively, which were forged and annealed at constant temperature for several days and then quenched in water. As shown in Fig. 1, for instance,
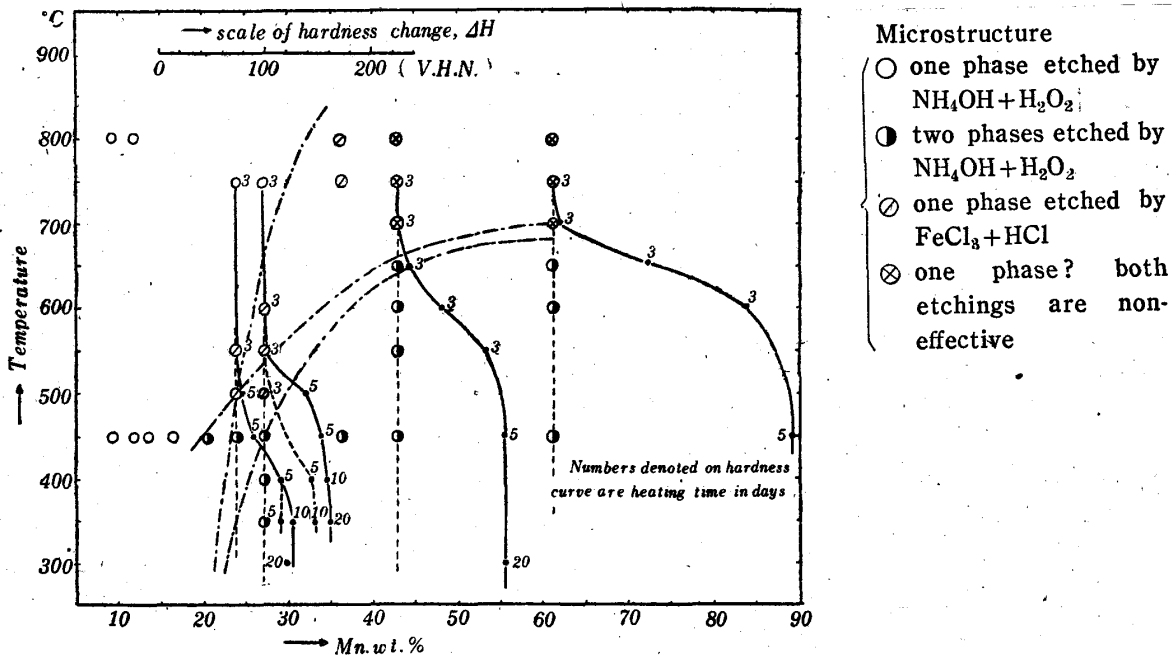

Microstructure
- O one phase etched by $NH_4OH + H_2O_2$
- ◑ two phases etched by $NH_4OH + H_2O_2$
- ⊘ one phase etched by $FeCl_3 + HCl$
- ⊗ one phase? both etchings are non-effective

Fig. 1 The hardness changes and microscopic structures of Cu-Mn alloys which were quenched from various temperatures after heating for several days. Three chain curves are the solubility limits proposed by Ishiwara, the authors and Grube, respectively from the top.

the hardness of the alloy containing 61.3 % of manganese and heat-treated below 650°C was remarkably higher than that heat-treated above 700°C for 3 days, it is, therefore, supposed that there may be a certain phase change between 650°C and 700°C. Similarly, other alloys may have phase change at the temperature at which a remarkable increase of hardness is indicated. Corresponding to these, changes in microstructures of the quenched alloys were also observable. Some of them are shown in Photos. 1~7. Photos. 1~3 show the structures of the alloy containing 27.2 % of manganese. Photo. 1 shows the structure quenched in water after heating for 5 days at 500°C, just below the temperature at which a sudden increase of hardness was shown. The structures, especially the grain boundaries of specimens quenched from the temperatures not lower than 500°C could not be etched by the solution ($NH_4OH + H_2O_2$), and it was necessary to etch them successively with the solution ($FeCl_3 + HCl$) as in Photo. 1. The specimens, which had precipitated the second phase of manganese at lower temperatures, could be etched only with the solution ($NH_4OH + H_2O_2$) as in Photo. 2. Photo. 3 shows the same structure as Photo. 2 etched successively with the solution ($FeCl_3 + HCl$), and the amount

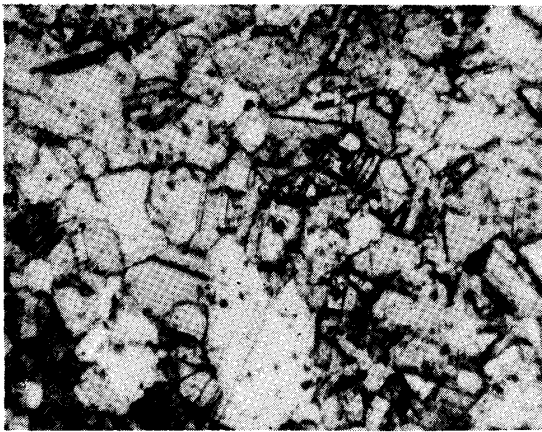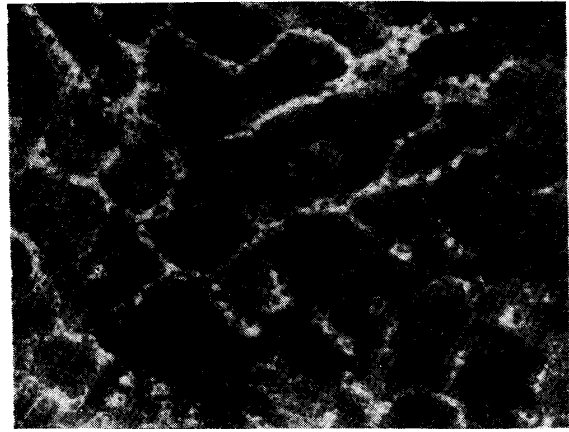Photo. 1 Mn 27.2 %, 500°×5 days, water quench., etched by $NH_4OH + H_2O_2$ and $FeCl_3 + HCl$,   ×400.

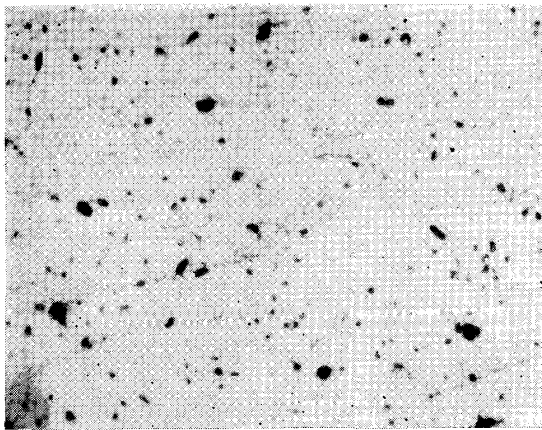Photo. 4 Mn 42.9 %, 650°×3 days, water quench., etched by $NH_4OH + H_2O_2$ and $FeCl_3 + HCl$,   ×400.

Photo. 2 Mn 27.2 %, 400°×10 days, water quench., etched by $NH_4OH + H_2O_2$ only,   ×400.
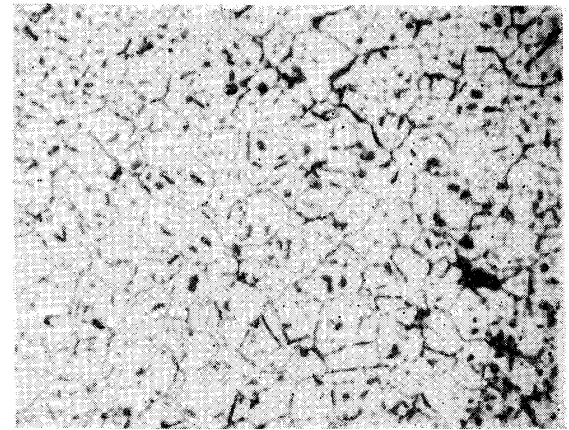
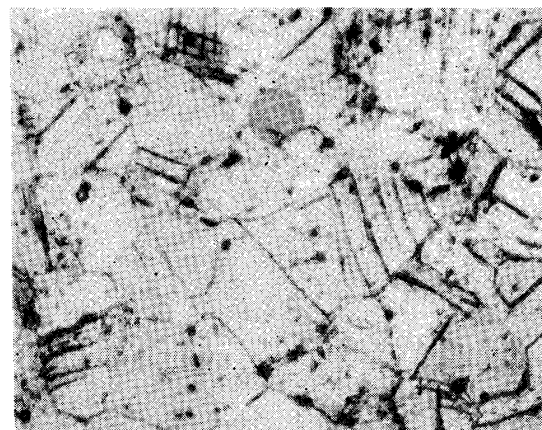Photo. 5 Mn 42.9 %, 550°×3 days, water quench., etched by $NH_4OH + H_2O_2$ and $FeCl_3 + HCl$,   ×400.

Photo. 3 Mn 27.2 %, the same as photo. 2, etched by $NH_4OH + H_2O_2$ and $FeCl_3 + HCl$,   ×400.

Photo. 6 Mn 36.3 %, 750°×3 days + 800°× 2.5 hrs., water quench., etched by $NH_4OH + H_2O_2$ and $FeCl_3 + HCl$,   ×100
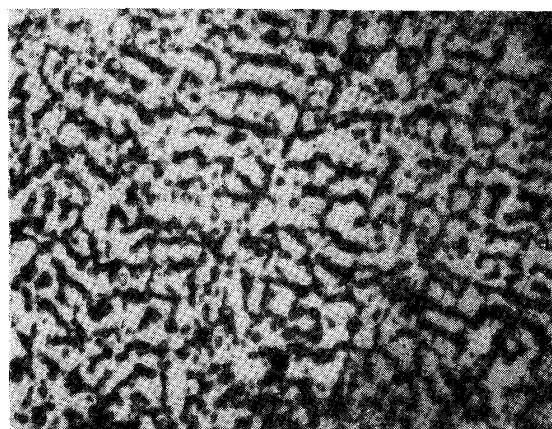
Photo. 7   Mn 61.3 %,   650°×3 days,   water
quench., etched by NH₄OH+H₂O₂
and FeCl₃+HCl,   ×400.

of the second phase precipitated was clearly larger than that in Photo. 1. For the alloy containing 42.9 % of manganese and heat-treated above 650°C at which the phase change occurred, both etching reagents were non-effective, because, in the case of the solution (FeCl₃+HCl) a hard brown film was produced on specimens immediately after dipping into solution, so that the microstructures were hardly inspected. This unfavourable feature also appeared in the alloy containing 61.3 % of manganese and heat-treated above 700°C. As shown in Photo. 6, the structures of alloys containing manganese up to 36·3 % could be distinguished without any difficulty. From the comparison of Photos. 2, 5 and 7, it will be noticed that the form of the second phase changes considerably with mangnese content. The condition shown in Photo. 1 should have been in the range of two phases according to Ishiwara-Isobe's diagram, but in the range of one phase according to Grube's diagram, and our results were rather allied with the latter, too. The condition of Photo. 6 ought
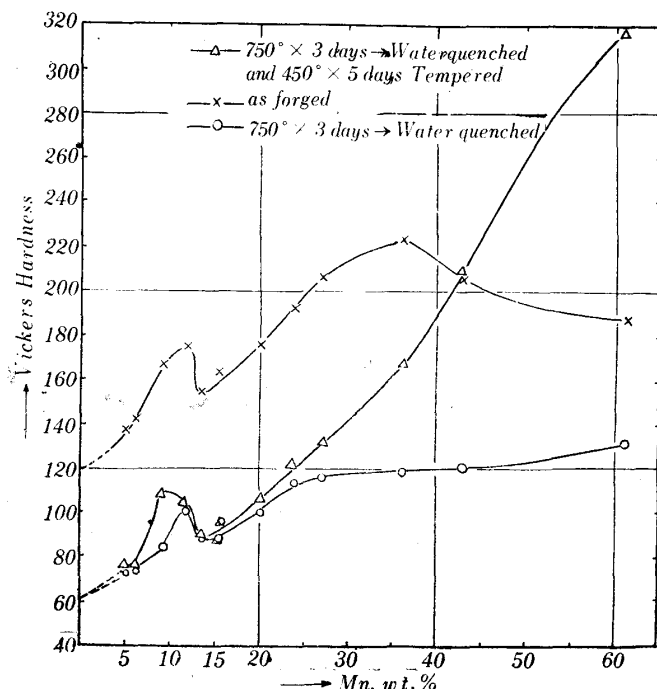

Fig. 2   The hardness changes of Cu-Mn alloys follow-
ing the three different heat-treatments.

to have two phase according to the former, but is of single phase according to the latter and so with our experiments. So Grube's type of the diagram can be said to be reasonable from the results shown in Fig. 1. But our solbility curve lay a little higher than Grube's one with the lowering of manganese content.

The hardness increase in specimens containing 5.15~ 61.3 % of manganese quenched in water from 750°C after heat ing for 3 days, was very gradual above 23.9 % as shown in Fig. 2. It was, perhaps, because of the cold work-

hardening by forging at comparatively lower temperatures that the absolute hardness values of forged alloys were very high, but the whole tendency of hardness change was similar to the quenched system, especially in the range of

lower contents of manganese. Then, the hardness of specimens tempered at 450°C for 5 days after quenching from 750°C, differed clearly from that of the quenched samples, at and above 20.27 % of manganese, as shown in Fig. 2. In other words . the solubility limit at 450°C may be in the neighborhood of 20.27 % of manganese, which fairly agrees with the results of microscopic experiments as shown in Fig. 1.

The anomalous points on the three curves in Fig. 2, i.e., the anomalies in alloys containing 9.38 % and 12.0 % of manganese will be discussed later with other results.

(2) Change of thermal expansion.

The total dilatation curves were first observed in seven alloys containing 6.22~ 36.3 % of manganese which had paticularly been slow-cooled as stated in II(1). The results are shown in Fig. 3(a). The total dilatation was carried out at the constant rate of 2~3°C/min up to 550°C for all samples except the one containing 9.38 % of manganese. Contrary to our expectation, no sign regarding the solubility
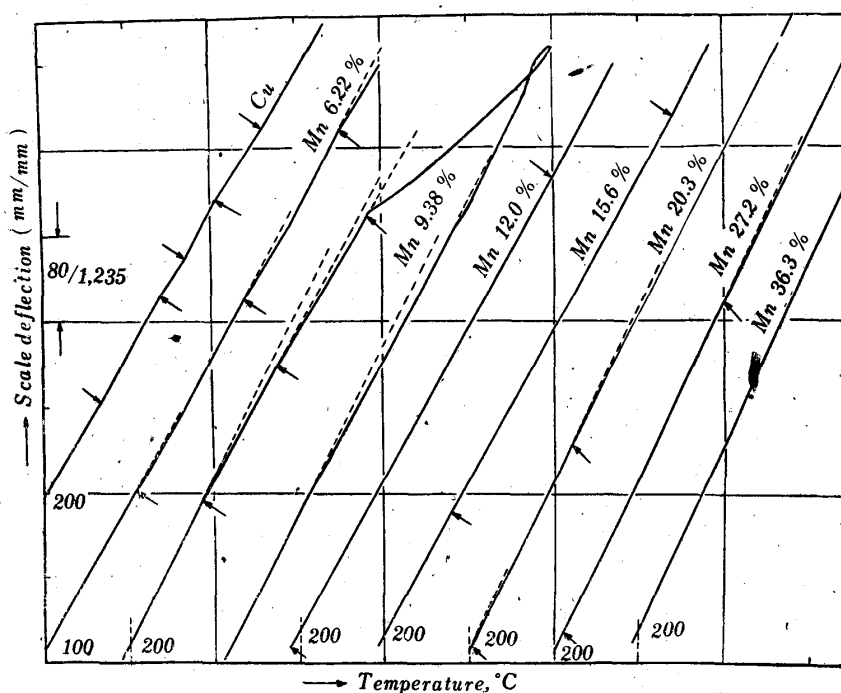

Fig. 3 (a) The total dilatation curves of pure copper and several Cu-Mn alloys.

change could be found on the dilatation curves even for the alloys containing more than 20.27 % of manganese. However, only the expansion coefficient of the alloy containing 9.38 % of manganese unexpectedly showed considerable decrease at about 490°C, indicating a certain irreversible behaviour in the process of the thermal hysteresis. Next, for all the samples that passed through the thermal procedure described above, the changes of differential dilatation were measured at the same rate of heating or cooling. In the present studies pure copper was used as the neutral sample. The results obtained are shown in Figs. 3(b) and 3(c). The decrease in the expansion coefficient at higher temperature was recognized in the alloys with lower content of manganese and was remarkable with the one
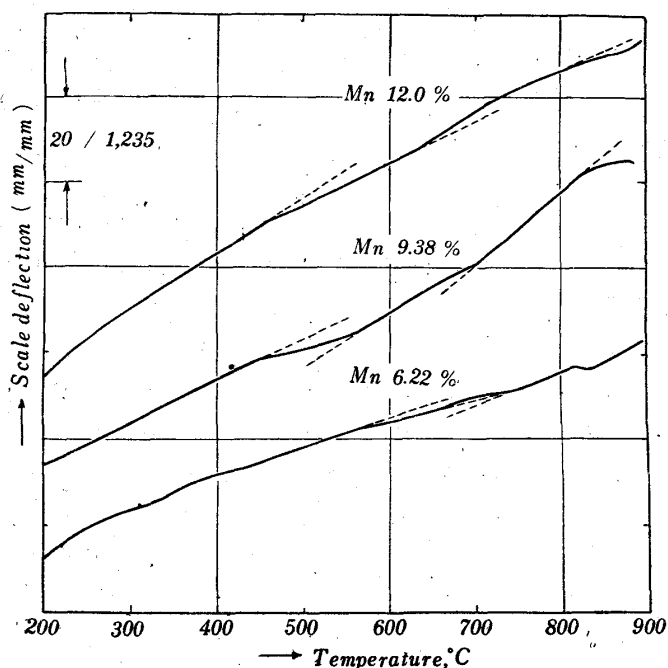
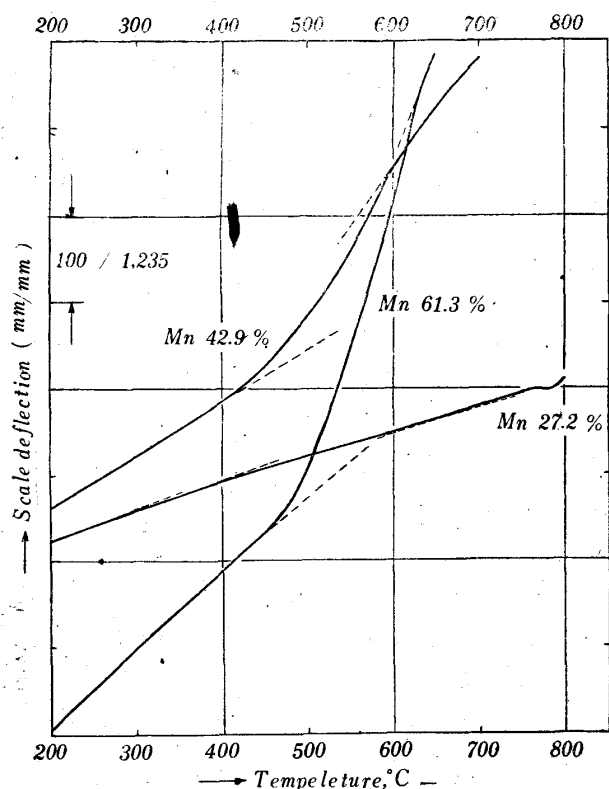Fig. 3 (b) The differential dilatation curves of several Cu-Mn alloys.

Fig. 3 (c) The differential dilatation curves of several Cu-Mn alloys.

containing 9.38 %. The critical temperature of such a change shifted not always in a simple manner with the change of mangnese content. But, such anomalies as exist even in the alloys containing less than 12 % of manganese, bear relations indeed to those observed on the hardness curves as shown in Fig. 2. The solubility change in the alloy containing 27.2 % of manganese was expected at 500~550°C, but on the expansion curve such a change is quite faint and rather a change closely related to what cccurred in the alloys of lower content was visible at about 500°C. On the other hand, in the alloys containing 42.9 and 61.3 %, the expansion curves differed from those mentioned above and the expansion coefficient increased rapidly at 400~450°C, followed again by a slow decrease at 600~650°C. These changes were almost reversible and took place during cooling process with a comparatively weak hysteresis of temperature. It was evident that these bear no relation to the solubility change because of the following reasons: (i) Notwithstanding the difference of content of manganese between two alloys being considerably large, the difference of the critical temperature in them was very small. (ii) The process of expansion or contraction in these transitions was opposite in meaning to that of the solubility change. Furthermore, a rapid decrease of expansion was recongnized at high temperature, say 800~900°C, but at present the reason for this phenomenon was not quite plain.

(3) Change of electrical resistivity.

The previous results by many workers concerning the dependence of electrcial resistivity on temperature showed considerable discrepancies, and, consequently, various conceptions have been put forward. As it was considered to be the most important reason for the above, that the irreversible hysteresis on the electrical resistivity vs. temperature curve was caused by the unfortunate formation of de-manganese layer on the surface of the sample heated up to higher temperature, the present experiments were carried out in a partial vacuum with CO_2 atmosphere with the constant rate of heating or cooling of 2~3°C/min. Thus, the results more satisfied than before were obtained as shown in Figs. 4 (a) and 4 (b). These samples were, of course, treated previously by the slow cooling method as mentioned in II (1). In the alloys containing manganese less than 36.3 %, the temperature coefficient of resistivity changed gradually from positive to negative, the negative tendency increasing with the increase of manganese content. These results agree qualitatively with those of Ishiwara[1] and Grube,[3] but radically disagreed with that of Satô.[6] Furthermore, if the curves are investigated in detail, it will easily be known that the curves over the range from room temperature to 800°C are not so linear as reported by Ishiwara, but have a series of bends corresponding to the variations in manganese content, as shown in Figs. 4 (a) and 4 (b) by arrow-heads, and the tendency of the change at lower temperatures relatively coincided with the results of Grube. In the alloy containing 9.38 % of manganese, however, a considerable hysteresis in temperature existed at the higher temperature range, changing the sign of the coefficient from negative to positive during heating process. It was considered that this anomaly was due to the same factors as that on the curve of hardness or thermal expansion at high temperatures. Such results have not yet been reported by any previous researchers. Corresponding to the change in the differential dilatation curves for both alloys containing 42.9 % and 61.3 % of manganese, the electrical resistivity showed a rapid increase at about 490°C on heating and a rapid decrease at about 400°C on cooling. This change was conceived not to be due to the solubility change for the same reason as stated in (2)(i). According to the explanation by Grube, who found the results similar to the above, the rapid increase of the resistivity at 400~450°C was simply attributable to the fact that the manganese atoms above such temperature would become more active in the matrix of the alloy. But if this proves to be the case, then, it can not be elucidated why the increase of resistivity gradually becomes weaker temporarily above 200°C than below. Also, because the activation energy of diffusion of manganese atoms was very smaller in the alloy containing 61.3 % of manganese than in the 42.9 % alloy as mentioned in the next section, Grube's conception could not be accepted as reasonable one. For these reasons, it is anticipated by the present authors that the change is not caused by a process based on the solubility change of Grube's type, but is another one, somewhat of

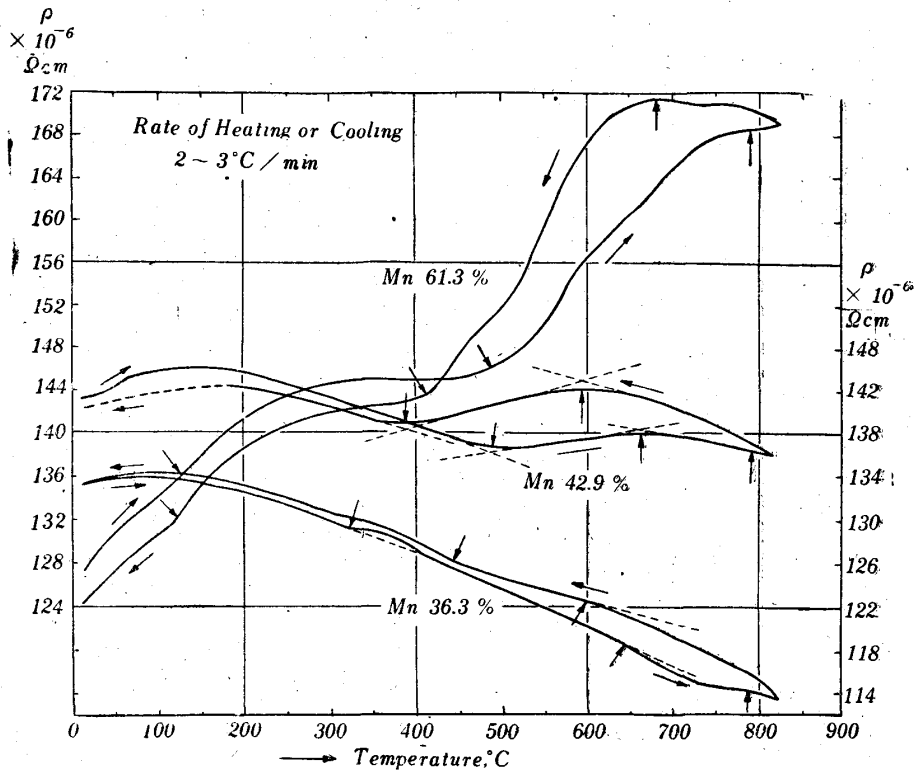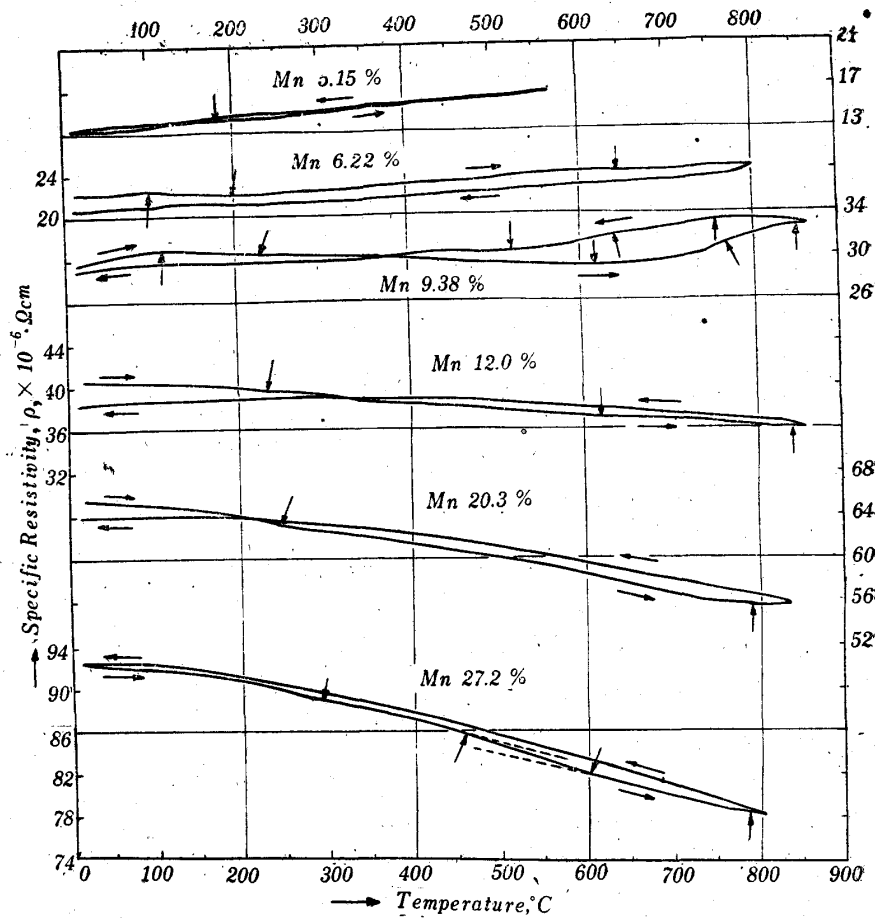(6) T. Satô; J. of Phys. Soc. of Japan, 5 (1950) No. 5, 287.

Fig. 4(a) and 4(b) Temperature dependence of electric resistivity of Cu-Mn alloys.

transformation type, taking place at the constant temperature regardless of composition in the heterogeneous region as shown in Fig. 1.

(4) Age-hardening after quenching and tempering.

The hardness changes and microscopic structures were examined in two alloys containing 42.9 % and 61.3 % of manganese, respectively, which were quenched in water from 750°C (a few samples from 800°C) after heating for 3 days and then tempered at several temperatures from 350° to 550°C. The results were shown in Fig. 5 (a). The type of hardening curves in the initial stage of aging was almost
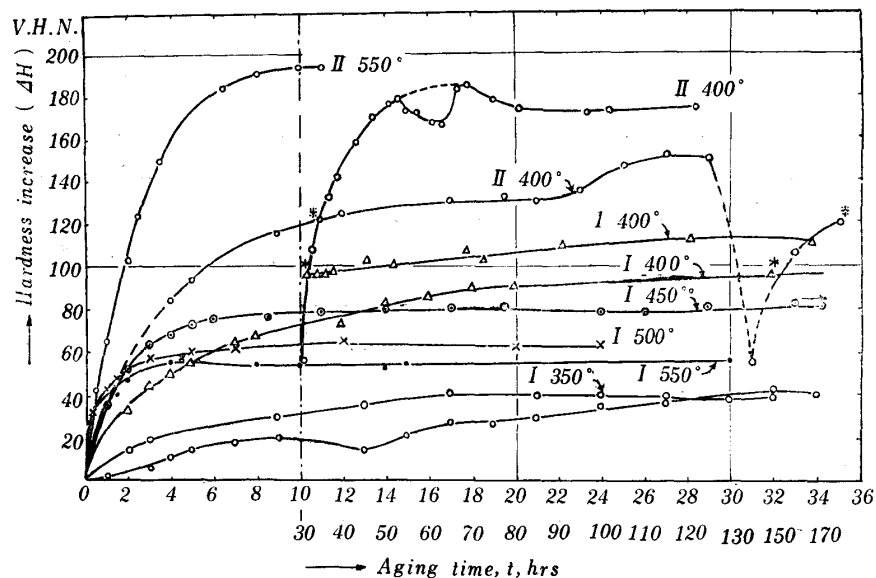

Fig. 5 (a) The age-hardening curves of I (Mn 42.9 % alloy) and II (Mn 61.3 % alloy) at various tempering temperature after quenching from 750°C.

in accordance with that of Austin-Rickett. If a general expression is adopted, it will be as follows :

$$\frac{p}{1-p} = Kt^n ,^{(7)}$$

and we obtain the value of n in the case of aging at 500°C in the alloy containing 42.9 % of manganese as follows :
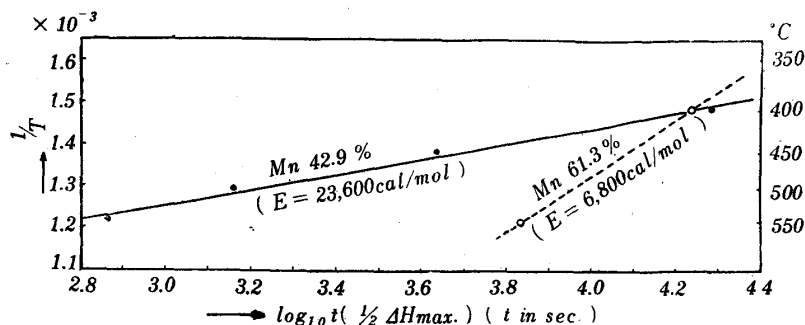
$$n = 0.98 \fallingdotseq 1,$$

Fig. 5 (b) Relation between $\log_{10} t$ (t is the time at half of the maximum hardening) and $1/T$ (T is the absolute aging temperature)

(7) Y. Mishima, R. Hasiguti and I. Obinata ; Kinzoku Gakkai-shi 12 (1948) 7~12, 16.

which suggests the type is of approximately the so-called pseudo-precipitation. But at other temperatures the values of n were a little deviated from 1, so the above formula could not hold strictly. Hence, the activation energy of age-hardening could not be calculated from the relation between $\log K$ and $1/T$ (T is absolute tempering temperature), and in the present work the calculation was carried out approximately by using the linear relation between $\log 1/t$ (t is the time for $p=$ 0.5) and $1/T$, as shown in Fig. 5 (b). The activation energy in the alloy containing 42.9 % of manganese was about 23,600 cal/mol, whereas the activation energy of diffusion of manganese atom in copper is 23,ʻ00 cal/mol.[8] The values of n in the alloy containing 61.3 % of manganese at 550° and 400°C were both about 1.09. The activation energy obtained only from two experiments were about 6,800 cal/ mol, much smaller than that of the former alloy. Hence, it should be taken into account that the diffusion of manganese atom takes place rather in the manganese rich alloy in the latter case. But, as to the lowering of activation energy, it is supposed to be more important than the above, that a more complex structure may exist in the heterogeneous phase with higher content of manganese. The structural changes during aging process are shown, for example, in Photos. 8 and 9. The precipitated phases in grains were shaped like needles or discs parallel,
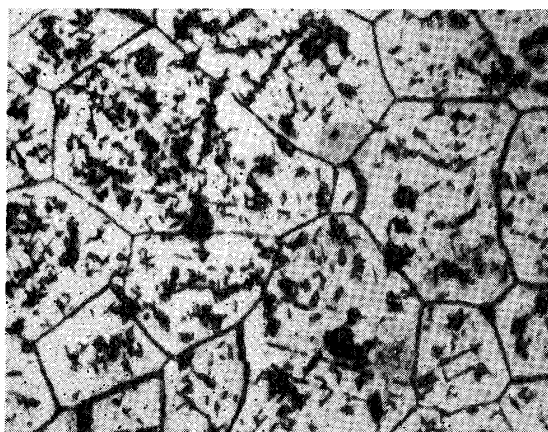

Photo. 8 Mn 61.3 %, 750°×3 days, water quenched and 400°×5 days tempered, etched by $NH_4OH+H_2O_2$ and $FeCl_3+HCl$,   ×400.

Photo. 9 Mn 42.9 %, 750°×3 days, water quenched and 450°×52 hrs. tempered, etched by $NH_4OH+H_2O_2$ and $FeCl_3+HCl$,   ×200.

perhaps, with certain crystallographic planes of mother crystals. These shapes in the alloy with 61.3 % manganese were different from that shown in Photo. 7, due, perhaps, to the quenching effect from 750°C in the specimens shown in Photo. 9.
(5) Variation of specific gravity and other properties.

The specific gravity of pure copper and of alloys containing various amount of manganese were measured by water-immersion metohd and the results are shown in Fig. 6 with those of other properties. As the specimen were cut off and machined from the hot-forged rods, the values obtained might be somewhat different

(8) W. Seith ; "Diffusion in Metallen" Berlin, (1939), 43

from the absolute one for each alloy, but it was first found that with 12~14 % of manganese a certain anomaly occurred, and then that with more than 36.3 % of manganese the change of specific gravity became fairly weak. Fig. 6 shows also the specific resistivity of each alloy at room temperature (12~14°C) and the mean value of linear expansion coefficient from 100° to 500°C or from 50° to 450°C. The curve of expansion coefficient vs. composition displays also the anomaly at 9.38 % of manganese.

Fig. 6 Specific gravity, expansion coefficient and specific resistivity of Cu-Mn alloys.

These phenomena could not be recongnized on the curve of specific resistivity which, however, shows characteristic bend with 23.9 % of manganese, and the gradual decrease with more than 36.3 % of manganese, respectively.
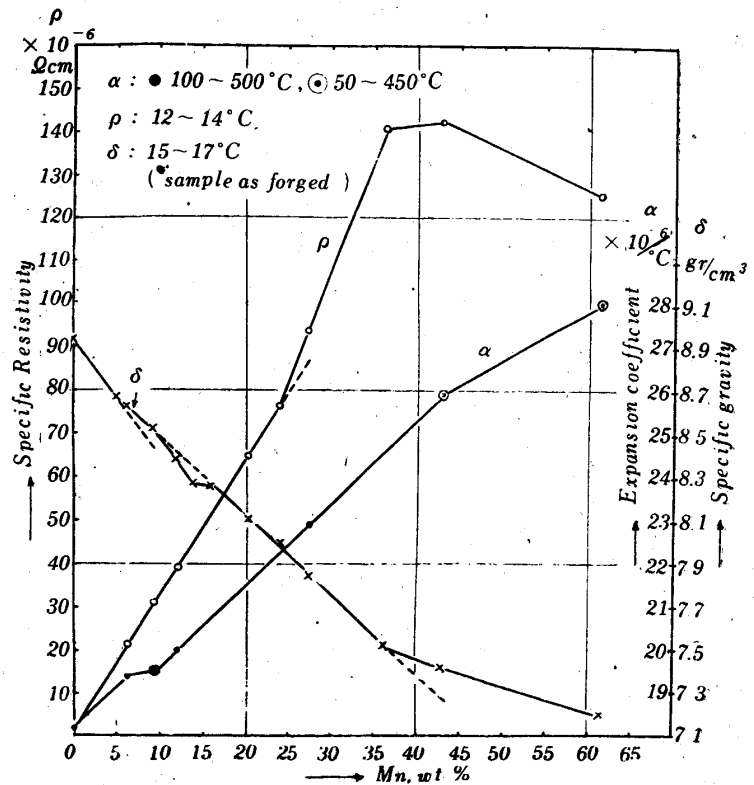
Summary and Conclusion

(1) The solubility curve of copper-rich solid solution of Cu-Mn system was proposed from microscopic and hardness experiments, which is of the same type as that of Grube but different from that of Ishiwara and Isobe. But in the lower content of manganese a slight difference in temperature was recognized between our results and Grube's.

(2) From the changes of thermal expansion and electrical resistivity, some anomalies at the higher temperature were observed in the alloy with 9.38 % of manganese and the particular changes were observed in the alloy of higher concentration such as 42.9 % and 61.3 %, which were considered to be due to a certain transformation type but not to a solubility change. So it was necessary to investigate the diagram more profoundly.

(3) The activation energy of age-hardening after quenching and tempering was about 23,600 cal/mol in the alloy with 42.9 % of manganese, whereas it was very small in the alloy of 61.3 %.

(4) From the relation between specific gravity and composition at room temperature or between the mean linear expansibility below 500°C and composition, similar anomalies were observed at about 10~12 %, although it was conceived to be a homogeneous solid solution.