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NASA TECHNICAL MEMORANDUM   NASA TM-77752

STUDIES ON COPPER ALLOYS CONTAINING
CHROMIUM (1st REPORT). ON THE COPPER
SIDE PHASE DIAGRAM

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1. Report No. NASA TM-77752	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle STUDIES ON COPPER ALLOYS CONTAINING CHROMIUM (1ST REPORT). ON THE COPPER SIDE PHASE DIAGRAM		**5. Report Date** December 1984
		6. Performing Organization Code
7. Author(s) Toshio Doi		**8. Performing Organization Report No.**
		10. Work Unit No.
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		**11. Contract - Grant No.** NASw 4004
		12. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		**14. Sponsoring Agency Code**

15. Supplementary Notes

16. Abstract

The specimens were prepared from vacuum-melted alloys, of high purity vacuum-melted copper and electrolytic chromium. The liquidus and eutectic point were determined by thermal analysis. The eutectic temperature is 1074.8° and its composition is 1.28 wt% of chromium. The deternunation of solid solubility of chromium in copper was made by microscopic observation and electrical resistivity measurement. The solubility of chromium in solid copper is 0.6 wt% at 1050°, 0.4 wt% at 1000°, 0.25 wt% at 950°, 0.17 wt% at 900°, and 0.10 wt% at 840°.

17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified and Unlimited	
19. Security Classif. (of this report) Unclassified	**20. Security Classif. (of this page)** Unclassified	**21. No. of Pages** 12	**22. Price**

STUDIES ON COPPER ALLOYS CONTAINING CHROMIUM (1st REPORT).
ON THE COPPER SIDE PHASE DIAGRAM.*
TOSHIO DOI

I. Introduction

Copper alloys containing chromium are used more recently for support wires
of vacuum tubes, conductive wires and some other parts as electrical materials
because of its high temperature resistance prop?rties and high mechanical
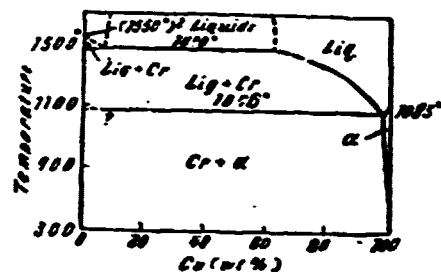strength in relation to its high electrical concuctivity.

Fig.1 Phase diagram of Cu-Cr alloy.

Before starting to study copper-chromium alloy, it is necessary to get a
two elements phase diagram of copper-chromium alloy. The phase diagram
of this alloy has been studied for a long time. The phase diagram in Fig. 1
is the data from Siedschlag (Reference 2) in the Metals Reference Book (Refer-
ence 1). This diagram shows the eutectic temperature of 1076°C and 1.5 wt%
of eutectic composition but its liquidus, solidus and the solid solubility
of chromium for copper are obscure. The phase diagram in the Metals Hand-
book (Reference 3) is almost the same as the diagram in Fig. 1 but it shows
1800°C as the melting point instead of 1550°C and the liquidus is changed.

**The Central Laboratory of Hitachi

* Announced at the convention of this society at Hiroshima in October, 1956.

This diagram was revised because Siedschlag (Reference 2) used impure chromium from the Thermit method for the test. The eutectic temperature and the eutectic composition in the report by the Copper Development Assn (Reference 4) (C.D.A for short) differ from the above mentioned data. There are reports from Corson (Reference 5), Alexander (Reference 6), Hibbard (Reference 7) and the C.D.A. (Reference 4) for the solid solubility of chromium for copper but as shown in Fig. 2, the properties are shown differently by the scholars.
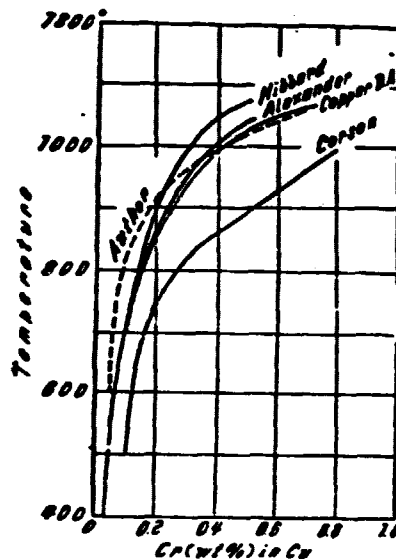

Fig.2 Solid solubility of chromium in copper.

As mentioned above, since the eutectic temperature, the eutectic composition and the solid solubility of chromium for copper of the two elements phase diagram of chromium copper alloy differ by scholars and also the liquidus and the solidus are obscure, it was decided to study the copper side phase diagram containing chromium up to 2 wt%, which is useful for industrial purposes, by using specimens which were prepared by a vacuum-melting method.

II. Specimens and Test Methods

1. Specimens

It is very difficult to produce Cu-Cr alloy containing certain amount of Cr because Cr has a strong affinity for O_2 and the melting point and specific

2.

gravity are different in Cu and Cr. At first the specimens have to be pre-
pared. In the methods tried recently, it is said that the method is the best
in which a sintered Cu-Cr mother alloy is added to the copp· melted in air
and cast rapidly. However, the technology of the vacuum melting method has
made progress in recent years. The author used vacuum-melted copper (Re-
ference 8) with more than 99.99% purity and electrolytic chromium of 99%
purity. They were melted in an Alandam heating furnace under pressure of
around 10^{-4} mmHg. Then it was cast in a water-cooled copper casting mold,
then an ingot was made with a very small amount of gas and some other im-
purities. After forging of this ingot, the specimen for thermal analysis
(12mm Dia. x 30mm Long) was prepared. Then the following specimens were
cold-drawn and prepared: the specimen for measurement of electrical poten-
tial drop by temperature (1mm Dia. x 200mm Long), the specimen for measure-
ment of electromotive force by temperature (0.5 mm Dia. x 1000mm Long),
the specimen for X-ray analysis (1mm Dia. x 500mm Long), the specimen for
microscopic observation of quenched specimen and for measuring electrical
resistance (1mm Dia. x 200mm Long). Table 1 shows the chemical composition
of the specimens.

Table 1 Chemical composition of samples.

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12
Cr (wt%)	0.09	0.10	0.29	0.31	0.53	0.56	0.81	0.84	1.02	1.05	1.22	1.82

2. Test Methods

The liquidus, solidus and the eutectic point were obtained from thermal
analysis. The solid solubility of copper for chromium was obtained from
measurement of electrical potential drop and electromotive force by tempe-
rature change, X-ray analysis, microscopic observation of quenched specimens
and measurement of electrical resistance. The details of the test are as
follows:

(1) Thermal Analysis

The specimen was put in a high purity alumina Tanman tube then the specimen
was melted in an electric smelting furnace. A sensor of Pt-PtRh thermocouple
was set to the center of the specimen and then thermal analysis was accom-
plished every 20 to 30 seconds during the cooling process by using a differ-
ential meter of electrical potential. Since the measured electromotive
force has to be converted to temperature, the same measurement was used

3.

for vacuum-melted copper and pure silver and the electromotive force and
the temperature corresponded to that of the vacuum melted copper and the
pure silver, which solidification points are 1083°C and 960.5°C respectively.

(2) Measurement of Electrical Potential Drop and Electromotive Force by Temperature Change

200 mA of direct current were applied to the specimens, which were annealed
at 650°C in a vacuum condition for 1 hour, to raise the temperature, then
electrical potential drop between two points which are 100mm apart was measu-
red continuously. Also a specimen was paired with a 0.5mm Dia. x 100 mm Long /339
piece of Pt then electromotive force was measured by raising its temperature
in a vacuum condition.

① Pt-PtRh
  Thermo couple
② Qartz tube
③ Gum
④ Sample holder
⑤ Nichrome wire
⑥ Water jacket
⑦ Geiser tube
⑧ Main cock
⑨ Leakage cock
⑩ Electric fur-
  nax
⑪ Sample
⑫ Water jacket
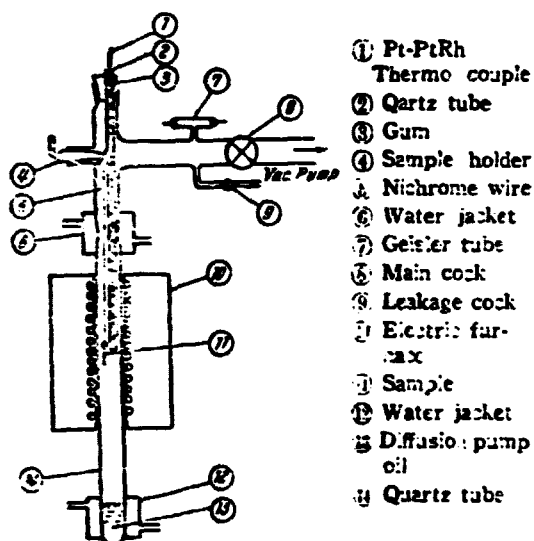⑬ Diffusion pump
  oil
⑭ Quartz tube

Fig.3 Vacuum-quenching apparatus.

(3) X-ray Analysis

To determine solid solubility of Cr for Cu, the specimens which were quenched
from a high temperature were investigated by a Cu characteristic X-ray of
the rear reflection method in which camera distance was 700mm.

(4) Microscopic Observation and Electrical Resistivity Measurement of The Quenched Specimens

To determine solid solubility of Cr for Cu, microstructure and electrical
resistivity of the specimens quenched from various temperatures was investi-
gated. As the first experiment, the specimens of Cu-Cr alloys containing
various compositions were heated at various temperatures from 600° to 1070°

for 24 hours with the vacuum-quenching apparatus as shown in Fig. 3. Then the specimens were quenched in oil. After quenching, the cross section of the specimens was corroded with copper chloride ammonium solution and then the microstructure was observed. As the second and third experiments, heat treatment was applied as shown in Fig. 4 then electrical resistivity was investigated and also the microstructure was investigated. The accuracy of the applied temperature was ±10°C.
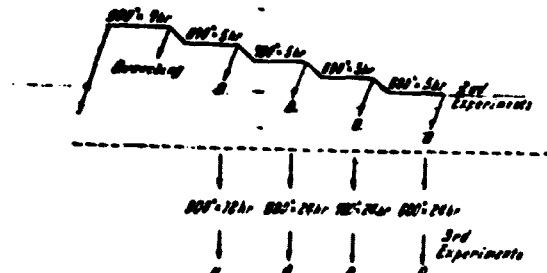

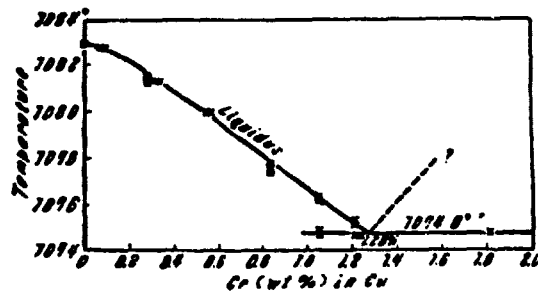Fig 4 Diagram of heat treatment.

III. Test Results and Concerns

1. Thermal Analysis

Fig. 5 Phase diagram of Cu-Cr alloy.

As shown in Fig. 5, the liquidus and the eutectic point well obtained with ±0.1°C of accuracy but the solidus was not obtained because of no clear appearance on the cooling curve of the electromotive force-time. The obtained liquidus can not be compared with past data since there is no details of the liquidus in the past data. The obtained eutectic point is 1074.8°C which is between 1076°C which Siedschlag (Reference 2) shows and 1070°C which the C.D.A. shows. The composition of Cr at the eutectic point was 1.28 wt% while Siedschlag (Reference 2) shows 1 to 2 wt% and the C.D.A. (Reference 4) shows 1.4 wt%.

2. Electrical Potential Drop and Electromotive Force by Temperature Change

As a sample, test results of the potential drop and electromotive force of Cu-0.56 wt% Cr alloy by temperature change are shown in Fig. 6 and Fig. 7. Any of the specimens containing various content of Cr do not show a transformation point clearly on both the temperature-potential drop curve and the temperature-electromotive force curve. Thus, solid solubility of Cr for Cu could not be obtained. It is impossible to determine the solid solubility with the above mentioned method because the test technique and test accuracy were not proper.
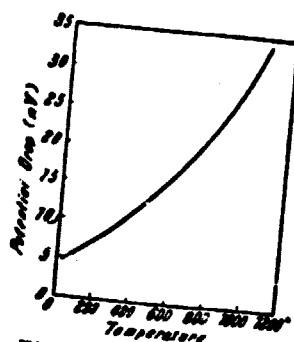
Fig.6 Potential drop of Cu-0.56(wt%)Cr alloy.

Fig.7 Electromotive force of Cu-0.56(wt %)Cr alloy-Pt couple.
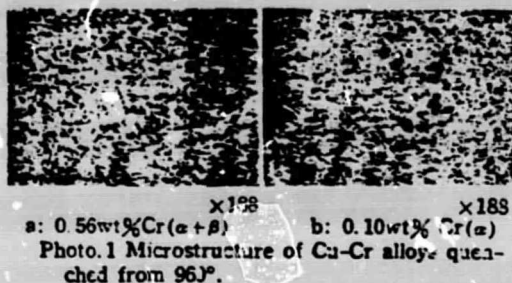
3. X-Ray Analysis

As the result of X-ray analysis, the specimens containing various Cr content and the vacuum-melted copper which was used as a standard specimen both showed the same, 3.615Å of grid constant.

The grid constant of a solid solution can be calculated from Vegard's law but the radius of the atoms are shown differently in books so, the results obtained

can not be compared. However, it is possible to determine the solid solubility
of Cr for Cu by improving accuracy 1 to 2 figures.

4. Microstructure of the Quenched Specimens and Electrical Resistivity

Photo 1 shows the microstructure of the Cu-Cr alloy which was quenched from
960°C as a sample.

×198   ×188
a: 0.56wt%Cr(α+β)   b: 0.10wt% Cr(α)
Photo. 1 Microstructure of Cu-Cr alloy quen-
ched from 960°.

"a" shows the α + β phase of the alloy containing 0.56 wt% of Cr and "b"
shows α phase of the alloy containing 0.10 wt% of Cr. The results of the
observed microstructure are shown in Fig. 8 and in the electrical resistivity
in Fig. 9. The solid lines show the test results of the second experiment
and the dotted lines show the results of the third experiment. In the second
experiment a single α phase was shown in only the specimens containing 0.10 wt%
of Cr which were quenched from 960°C and 870°C. The other specimens had a
α + β phase. For the specimen containing 0.29 wt% (0.355 at%) of Cr which
was quenched from 960°C, it was difficult to determine whether it has a single
α phase or an α + β phase.

The relationship between electrical resistivity and at% of Cr at a certain   /340
temperature was linear in the α+β phase. There must be a transition point
on the border of the α phase. As shown in Fig. 9, the test data shows an
approximate linear relationship between 0.29 wt% (0.355 at%) Cr and 1.06 wt%
(1.31 at%) Cr which were quenched from 960°C and 870°C but 0.10 wt% (0.122 at%)
Cr is out of the linear line. Thus, it is presumed that the specimen contain-
ing 0.10 wt% (0.122 at%) Cr and quenched from 960°C and 870°C have a single
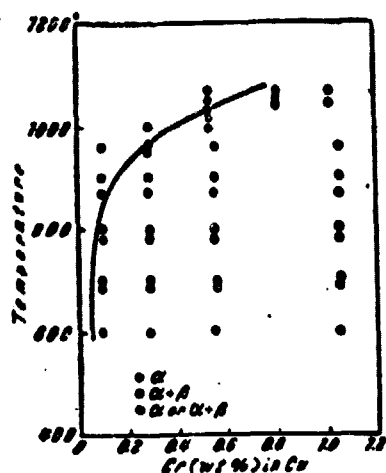phase.

Fig. 8 Solid solubility of chromium
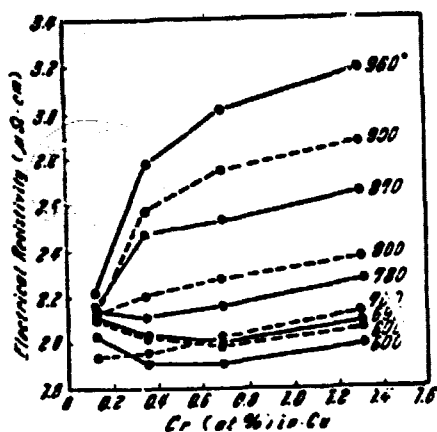in copper.

Fig. 9 Effect of quenching temperature
upon the electrical resistivity of Cu-
Cr alloys.

As mentioned above, the results from microstructure observation and the measurement results of electrical resistivity are consistent. Therefore, the results of the microstructure observation of the specimens which were quenched from 780°C or less should show an $\alpha + \beta$ phase so, the relationship between the electrical resistivity and at% of Cr for each quenching temperature should be linear. But the result from the specimens containing a low concentration of Cr are not on the line. Because in the alloy containing a low concentration of Cr, it is hard to get an equilibrium condition at a lower quenching temperature. Since it was considered that the time of heat treatment was too short in the second experiment (upper portion of Fig. 4), the third experiment (lower portion of Fig. 4) was performed. As the results of the microstructure observation of the specimens from the third experiment, 0.10 wt% (0.122 at%) Cr alloy which was quenched from 900°C shows a single α phase and all of the others show an $\alpha + \beta$ phase. On the other hand, the

8.

measurement results as the dotted line shows in Fig. 9, of electrical resistivity of the specimens quenched from 900°C to 700°C are consistent with the microstructure observation. The specimens quenched from 600°C of 0.10 wt% (0.122 at%) Cr and 0.29 wt% (0.355 at%) Cr seem that the time of heat treatment was too short.

From the above test results, the solid solubility of Cr for Cu was determined as the solid line shows in Fig.8, i.e. 1050°C at 0.6 wt%, 1000°C at 0.4 wt%, 950°C at 0.25 wt%, 900°C at 0.17 wt% and 840°C at 0.10 wt%.

To compare with the past data, the author's results were plotted in Fig.2. The author's curve in the range of less than 900°C is slided to the low concentration side and in the range of more than 1000°C, it is slided to the high concentration side compared with the curves of Hibbard (Reference 7), Alexander (Reference 6) and the C.D.A. (Reference 4).

The summarized phase diagram of Cu-Cr alloy on the Cu side by the author is shown in Fig. 10.
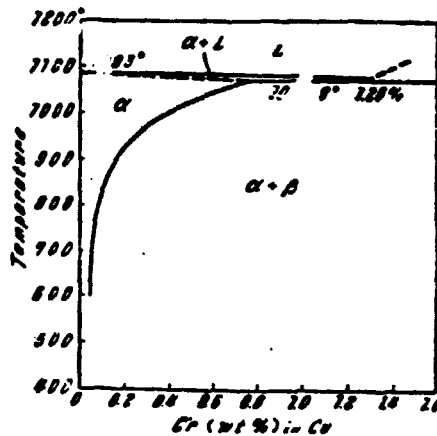

Fig. 10 Phase diagram of Cu-Cr alloy by author.

IV. Conclusions

To study the previously announced phase diagrams of the two elements Cu-Cr alloy on the Cu side, thermal analysis, measurement of electrical potential drop and electromotive force by temperature change, X-ray analysis and microstructure observation and measurement of electrical resistivity of quenched specimens were accomplished. As the results, a new phase diagram shown in Fig. 10 was obtained with the accuracy of ±0.1°C for liquidus and eutectic temperature and ±10°C of solid solubility of Cr, i.e. the eutectic temperature is 1074.8°C, the eutectic composition is 1.28 wt% Cr, the solid solubility of Cr for Cu is 1050°C at 0.6 wt%, 1000°C at 0.4 wt%, 950°C at 0.25 wt%,

900°C at 0.17 wt% and 840°C at 0.10 wt%.

In conclusion, the author thanks Takejiro Murakami, an honorary professor of Tohoku University and Shigeyasu Koda, a professor of Hokkaido University for their cordial guidance and encouragement and also the staff of this company for giving an opportunity for this experiment.

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