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The Age Hardening of Silver with Copper-Silicide

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with
COPPER-SILICIDE

By

Joseph Edward Shaw

Butte, Montana

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

MONTATA SCHOOL OF MINES

BUTTE, MONTANA

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Introduction

The successful application of the phenomenon of precipitation hardening to aluminum and copper has indicated the possibility of hardening all metals in the same way. The phenomenon of age hardening was discovered by Wilm1) in 1911, and since that time much research has been carried on in all parts of the world on various alloy systems.

Due to the fact that sterling silver and silver plate are easily scratched or dented, it is evident that some such hardening of silver is desirable. Silver has been hardened by a number of hardening elements, among which are: copper and aluminum, cadmium, copper and cadmium, palladium and copper, silicon, copper and silicon, zinc, copper and zinc, copper and magnesium, copper and antimony, magnesium and zinc, and cadmium and antimony.2)

In this work copper-silicide, Cu_3Si, was used as the hardening constituent. In "The Constitution of the Copper-silicon System," Smith3) did not find this compound to exist in the free state, however, the two alloying elements were used in a ratio to produce a phase, Cu_3Si.

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1) A. Wilm Metallurgie 8, 225, (1911)
2) Loc. Cit.
3) C. S. Smith, "The Constitution of the Copper-Silicon System." Tr. A.I.M.E., Inst. Metals Div., 439 (1929)

Theory of Age Hardening

The theory of age hardening was proposed by Mercia,[4)]Waltenberg and Scott.[5)]The conditions necessary for age hardening seem to be the formation of a solid solution with a variable alpha range, in which the solute becomes more soluble at higher temperatures.

In such an alloy, which may be a true binary or a pseudo-binary system, the solid solution is heated in the homogeneous alpha field and then quenched, leaving a super-saturated solution which retains its homogeneity at room temperature. Annealing at some temperature below the solubility curve causes the solute to be thrown out of solution in fine submicroscopic particles dispersed along the planes of slip. These particles, either by slip interference[6)]or lattice distortion, produce the hardening effect.

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4) Mercia, "The Age Hardening of Metals." Tr. A.I.M.E. 99, 13 (1932)

5) Mercia, Waltenberg, Scott, U. S. Bur. of Stds. Sci. Paper 347 (1919)

6) Jeffries and Archer, "The Slip Interference Theory of Hardening." Chem. and Met. Eng., 24 (1921)

Experimental Work

The alloys were prepared from pure silver, electrolytic copper and silicon. All melts were made in a carbon resistor electric furnace, and all annealing was done in an electric tube furnace, the temperature of which was controlled by a rheostat. Graphite crucibles were used for all melts. Fusion temperatures were measured with an optical pyrometer, and annealing temperatures were measured with a platinum thermometer.

Copper-silicide was first made by melting together copper and silicon in the correct proportions to form the compound, Cu_3Si. (12.85% Si and 87.15% Cu) Several pieces of charcoal were placed on the charge to prevent it from oxidation. After a proper length of time sufficient to insure homogenity, the charge was removed from the furnace and allowed to cool. A weighed portion of the melt was then analyzed for Cu_3Si.

The silver alloys were then prepared by melting together silver and copper-silicide. After solidifying, the alloy buttons were annealed for one hour at 800° C. and quenched to do away with the effect of fractional solidification. The specimens were hammered and rolled into strips with hand rolls, the strips being cut into small pieces for individual treatment.

Hardness

The small individual strips were again annealed at 800° C. for one hour and quenched. This procedure removed the effects of cold work and assured a super-saturated solid solution at room temperature. 800° C. was found to give more consistent results so was used as the temperature from which to quench in all of this work.

Now, heating the alloy to some temperature below the solubility curve caused precipitation of the solute, thereby producing the hardening effect. For each temperature selected the hardness of the specimen was tested at regular intervals.

Hardness measurements were made on a Rockwell superficial hardness tester, using a 15 kilogram load and a one-sixteenth inch ball. Due to the fact that precipitation and agglomeration of particles do not take place at the same rate of velocity, the hardness measurements vary over a range of three or four points. This variation gradually decreases until complete precipitation is had, after which the softening is consistent.

Upon annealing the alloy at 500° C. it was found that the maximum hardness obtained was below that obtained at lower temperatures. The cause of this is that the rate of agglomeration of the particles is much faster than the rate of precipitation, and the size of the particles becomes too large in a very short time to give a maximum hardness. On annealing at higher temperatures the maximum hardness was obtained in one or two minutes, while at lower temperatures the maximum hardness was not obtained so soon. The longest time required to obtain the maximum hardness was about twenty minutes, and the hardness persisted over longer periods of time when aged at these lower temperatures.

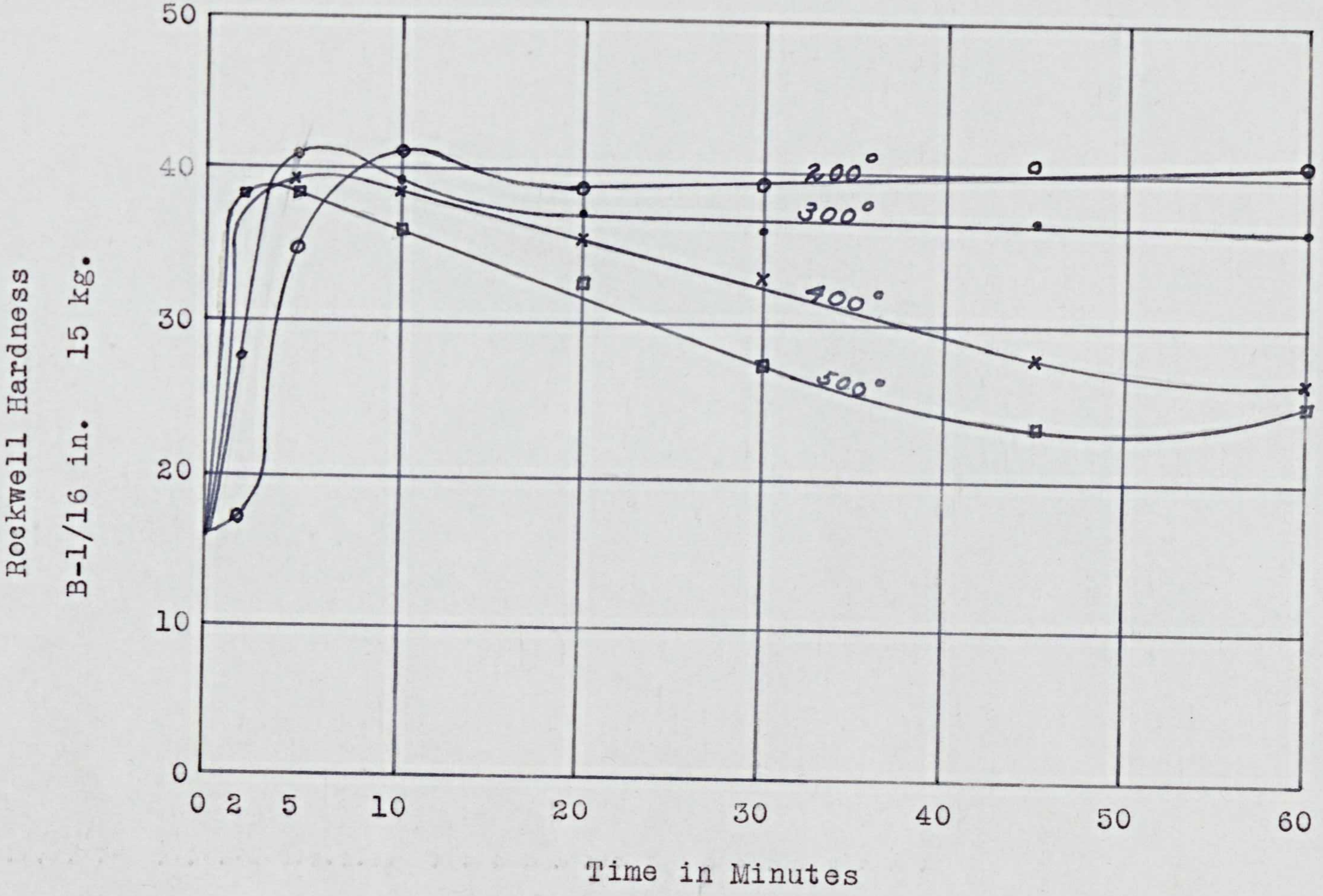
The maximum hardness obtained for any specimen was on the 2.5% Cu_3Si alloy upon aging for twenty minutes at 200° C. This hardness was about 43 on the scale used. The rate of hardening was found to be related to the temperature, that is, the higher the temperature the less time needed to get the maximum hardness. If the temperature was too high, however, the maximum hardness was not obtained.

This alloy system seems to be an exception to the general rule. In most of the systems that exhibit the phenomenon of age hardening, the maximum hardness obtainable increases with the amount of hardening agent used up to a certain point, being different for each system. The maximum hardness obtained for each alloy investigated was very nearly the same, being between 38 and 42 on the scale used. Although the hardness does not increase, the alloys become more brittle and much harder to work as the amount of hardening agent is increased. Upon annealing the specimens in air they became oxidized and disintegrated, and rolling was found to be very difficult. A reducing atmosphere was found to prevent these difficulties, however, this was discovered too late to be used in this work.

TABLE I-Change In Hardness with time at Various Temperatures

Alloy No. 1 (95% Ag, 5% Cu_3Si)

Reheating Temp. Degrees C.	Reheating Time in Minutes	Rockwell Hardness 15 kg. Load
As Quenched	0	16.3
200	2	17.1
200	5	34.6
200	10	41.0
200	20	38.9
200	30	39.3
200	45	40.7
200	60	40.1
As Quenched	0	16.3
300	2	27.2
300	5	40.8
300	10	38.2
300	20	37.4
300	30	35.9
300	45	36.4
300	60	35.8
As Quenched	0	16.3
400	2	37.0
400	5	39.4
400	10	38.6
400	20	35.0
400	30	32.1
400	45	27.5
400	60	25.7
As Quenched	0	16.3
500	2	38.2
500	5	36.8
500	10	35.4
500	20	32.1
500	30	26.4
500	45	23.0
500	60	24.7



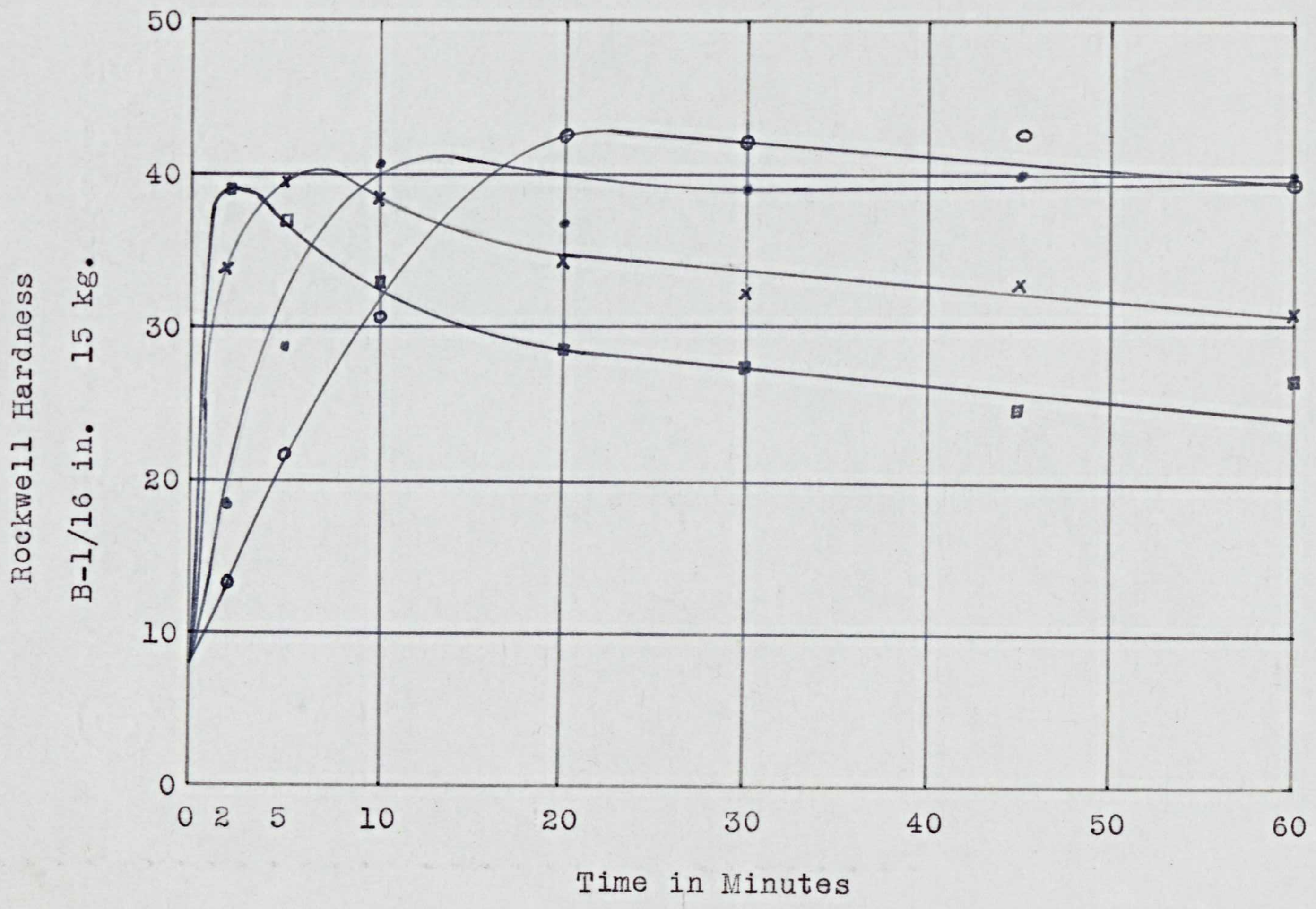
Change in Hardness on Reheating Alloy Ag + 5% Cu_3Si

TABLE II-Change in Hardness with Time

at Various Temperatures

Alloy No. 2 (97½% Ag, 2½% Cu_3Si)

Reheating Temp. Degrees C.	Reheating Time in Minutes	Rockwell Hardness 15 kg. Load
As Quenched	0	8.5
200	2	12.4
200	5	21.2
200	10	30.7
200	20	42.8
200	30	41.7
200	45	42.1
200	60	39.4
As Quenched	0	8.5
300	2	18.4
300	5	28.9
300	10	40.3
300	20	36.8
300	30	39.4
300	45	40.0
300	60	39.6
As Quenched	0	8.5
400	2	33.4
400	5	39.8
400	10	38.6
400	20	34.7
400	30	31.9
400	45	32.8
400	60	30.7
As Quenched	0	8.5
500	2	39.2
500	5	36.1
500	10	32.4
500	20	28.9
500	30	27.3
500	45	24.8
500	60	26.4



Change in Hardness on Reheating Alloy Ag + $2\frac{1}{2}\%$ Cu_3Si

Conclusions

Silver can be age hardened by the addition of copper-silicide. The hardness increases rapidly at annealing temperatures between 200° C. and 500° C. The maximum hardness was obtained after aging for twenty minutes at a temperature of 200° C. Continued aging at this temperature caused a decrease in the hardness of the alloy due to agglomeration of the hardening constituent. An increase in the copper-silicide content above 2.5% fails to give an increase in the hardness of the alloy

Suggestions for Future Work

The determination of the position of the solubility curve would aid greatly the future work on this alloy. A reducing atmosphere seems to be necessary for all annealing and aging to prevent disintegration and oxidation of the specimens. As the maximum hardness was obtained at the lowest temperature tried, it seems logical that even lower temperatures should be tried. An alloy containing a lower percentage of copper-silicide may even be desirable.

I wish to acknowledge the help and guidance of Dr. Curtis L. Wilson, head of the Metallurgy Department at the Montana School of Mines, under whose supervision this work was performed, and who also aided with the writing of this thesis.