ISOTOPIC EXCHANGE BETWEEN Cu-Zn ALLOYS AND Zn^{++} IONS IN SOLUTION

by

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Introduction.

Recent experiments on isotopic exchange between metals and their ions in solution[1] have shown that under certain conditions it is possible to distinguish between two classes of metals: metals like Pb, Zn and Cd, the exchange of which is intensive, and the transition metals, which exchange weakly. It seemed interesting to extend this study to binary alloys containing metals of both classes. In this paper the results from the isotopic exchange between Zn^{++} ions and Cu-Zn alloys of various compositions are indicated and a tentative explanation presented.

Experimental.

The alloy samples were prepared from high-purity metals by vacuum melting in the following manner: in order to prepare samples of a given concentration both constituents were weighed after being repeatedly rinsed in acetone and bi-distilled water and dried in a jet of hot air. They were then placed inside a quartz tube connected to a high-vacuum system and heated to allow the degassing of the metals. This was checked by means of a Pirani gauge. When the pressure reached the order of 10^{-5}mm Hg the quartz tube was sealed off encapsulating the metals in-vacuo. The capsules were then placed in a vertical oven at 1200° C and after the metals were molten the capsules were taken out and agitated to provide for the recovery of the metal film deposited on the walls, and then quenched in cold water. The samples were then removed from the capsules and cut into dices of 1 cm^2 area and thermally treated at 300° C for 24 hours. The top surface was then mechanically polished with emery paper down to the finest grain and the remaining surfaces painted with Epodur, which was allowed to set at 60°C for a few hours. The choice of the protecting resin was made by testing the absorption of activity of several available brands. This particular resin, after being immersed for 30 minutes in Zn SO$_4$ solution, 0.5 M pH - 5, containing about 10^6 counts per minute of Zn^{65}, showed an activity of 2 counts per minute.

The next step was to take x-ray diffraction spectra of the alloys using a Norelco diffractometer equipped with a scanning Geiger counter and recorder. The method used was the same as for

powder specimens. The graphs obtained were analyzed and the lines checked against A.S.T.M. cards, thus identifying the phases.

A 0.5 M solution of Zn SO_4 was prepared using P.A. grade reagent and bi-distilled water, the pH set to the order of 5, and about 0.1 millicuries of Zn^{65} (beta, gamma, period: 245 days) added in the form of Cl_2 Zn.

The gamma-ray spectrometer used for the activity measurements was a Baird Atomic with a NaI(Tℓ) well-type scintillation crystal. Spectra of the Zn^{65} source were made and one of the lines chosen that gave the best activity-to-background ratio. All measurements were made over extended times so as to minimize the errors due to fluctuation.

The temperature control was achieved by means of a circulating water thermostat. Two containers were adapted in series to the thermostat, one with the activated solution and the other with bi-distilled water where the samples awaited being transferred to the solution, thus avoiding any temperature lag. The handling of the samples was made with resin-protected tweezers.

To determined the kinetics of the exchange the samples were taken out of the thermal bath and immersed in the activated solution for predetermined times (the solution being violently stirred), rinsed carefully in acetone and bi-distilled water, dried in a jet of hot air and their activity measured in the gamma-ray spectrometer. Measurements of the activation energies of the process were performed in a similar way only varying the temperature.

Results and discussion.

Our results show that until 67Wt% Zn the alloy acquires practically no activity, behaving more or less like pure copper. At 67Wt% Zn there is a sudden transition and the alloy then shows the activity of the order of magnitude of that of pure zinc. The x-ray diffraction spectra of the alloys indicate that the transi tion coincides with the appearance of the epsilon phase. On the other hand, measurements of the activation energies of the proc- ess gave for the alloys below 67Wt% Zn 2900 cal/mol and for above that value 1900 cal/mol.

To verify the reversibility of the process the alloys were irradiated by neutrons in the reactor at the Instituto de E nergia Atômica, São Paulo, and then exchanged with inactive $ZnSO_4$. It is certain that simultaneous processes such as adsorption of ions from the solution, etc., mask the pure process of exchange. However, by this method we confirmed the existence of the transi tion at 67Wt% Zn.

To explain this transition in the isotopic exchange we used the Tammann order-disorder theory[2] to the effect that the Zn atoms in the alloy would exchange more or less depending on wheth er their nearest neighbours be Zn or Cu atoms. This was done on the assumption that the Cu-Zn binding is stronger than the Zn-Zn binding. Up to 37.5Wt% Zn (alpha phase) each atom has 12 nearest neighbours and since this phase is disordered, the probability of occupation of the 12 sites around a Zn atom is equal for both Cu and Zn. Since the concentration of Zn is small in this phase, in

average the Zn atoms are shielded by many Cu atoms and the exchange is weak.

The beta phase (up to 50Wt% Zn) is ordered in such a way that each Zn atom is always shielded by 8 Cu atoms. Similarly for the gamma phase (up to 67Wt% Zn), which is also ordered and with the same coordination. Both in the beta and gamma phases the exchange is negligible.

Above 67Wt% Zn the epsilon phase (disordered, coordination: 12) begins to appear. Since the concentration of Zn is high and each Zn atom is surrounded by 12 other atoms, mostly Zn, the exchange is increased. Similarly for the eta phase up to pure Zn.

References.

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2. G. Tammann, A Text Book of Metallography, The Chemical Catalog Company, Inc., New York, 1925.

3. A. Phillips and R. M. Brick, Handbook of Metals, American Society for Metals, 1958.
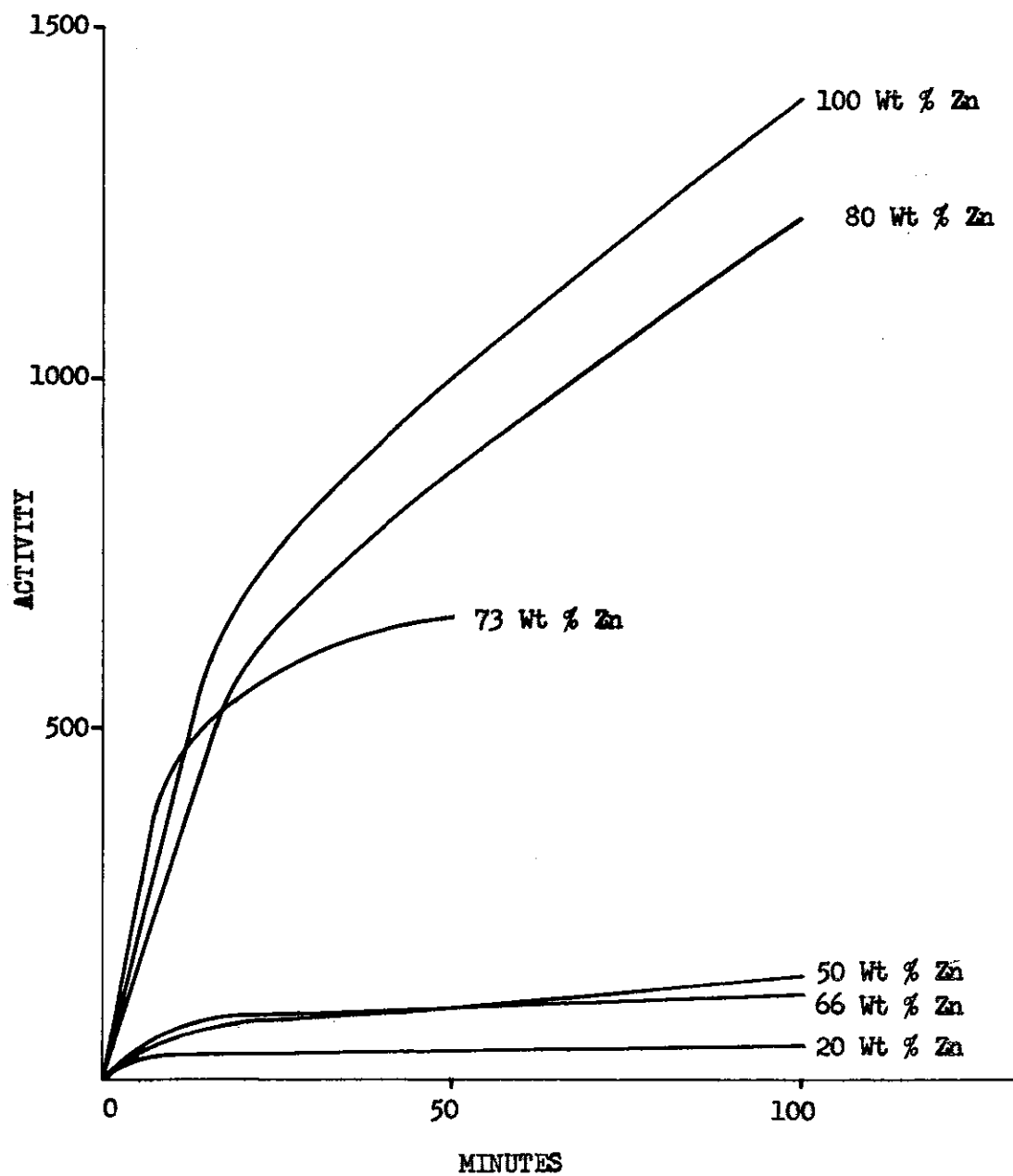
* * *

1500 —

1000 —

500 —

ACTIVITY

100 Wt % Zn

80 Wt % Zn

73 Wt % Zn

50 Wt % Zn
66 Wt % Zn
20 Wt % Zn

0   50   100

MINUTES

Fig. 1 —   Kinetic curves of the activity shown by different Cu-Zn alloys

after immersion in a Zn SO$_4$ 0,5M , pH–5 solution at 26.6° C.

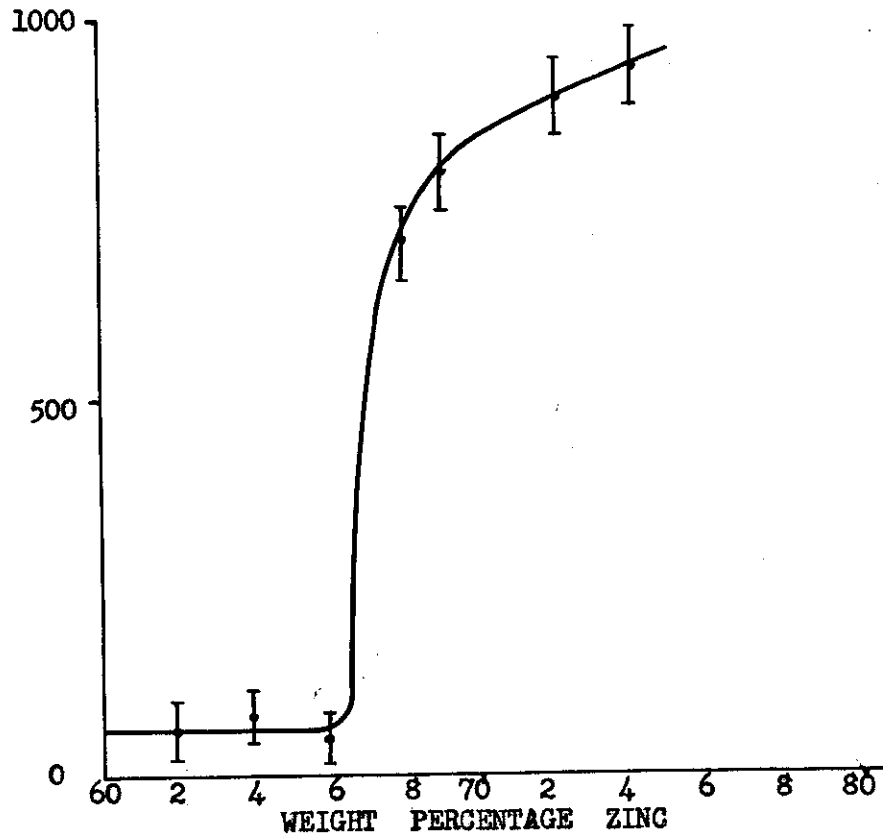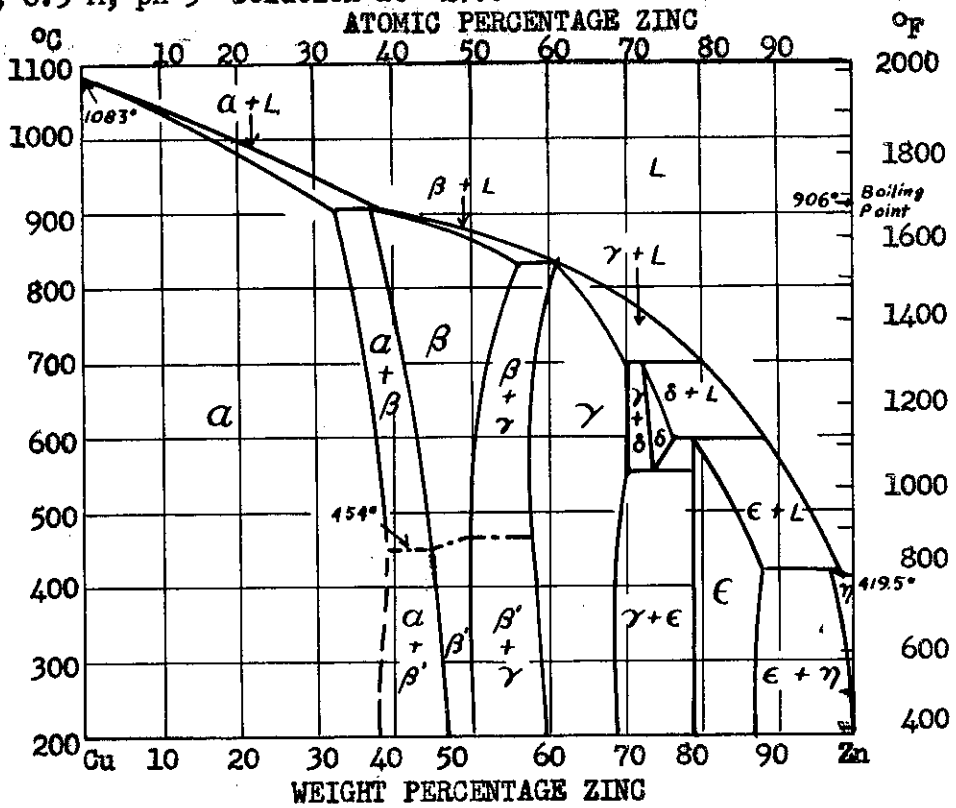Fig. 2 - Activity shown by different Cu-Zn alloys after 30 minutes immersion in a Zn SO$_4$, 0.5 M, pH=5 solution at 27.0° C.

Fig. 3 - Equilibrium diagram of Cu-Zn alloys [3].

Phase	Percentage Zinc	Crystal Structure
α ··········	0	Face-centered cubic
α ··········	37.5	Face-centered cubic
β ··········	45.5	Body-centered cubic
β ··········	50.0	Body-centered cubic
γ ··········	58.5	Cubic, low symmetry
γ ··········	67.5	Cubic, low symmetry
ε ··········	Saturated at 200 C	Close-packed hexagonal
η ··········	97.4	Close-packed hexagonal
η ··········	100	Close-packed hexagonal

Table 1 - Crystal structures of Cu-Zn alloys[3].