BEHAVIOR OF ACETYLENE UNDER HIGH PRESSURES IN PRESENCE OF COPPER OR COPPER ALLOYS

By Hiroshi Teranishi

Introduction

Since the year of 1898 when Erdmann and Koethner[1] reported that acetylene, in contact with copper or copper oxides at 230°C, polymerized and formed yellow brown products (cuprene), many works have been reported on the formation and properties of the cuprene, and in 1950 Léger and Quellet[2] reported on the kinetic investigation on the formation of cuprene from acetylene catalyzed by a copper wire. These have been, however, investigations on acetylene under atmospheric or lower pressures. As for acetylene under high pressures, Kinoshita[3] has observed, in our laboratory, the polymerization of acetylene on the inner surfaces of a steel vessel at the temperatures above 200°C, and recently Kiyama, Osugi and Kusuhara[4] have performed the kinetic investigation on the cuprene formation in the presence of variously annealed copper plates. On the effects of copper alloys to the behavior of acetylene at elevated temperatures, nothing has been reported in literature and some uncertainty has been brought to the knowledge on materials for handling acetylene under high pressures.

Therefore in the present paper, the author will report the behavior of acetylene under high temperatures (220~260°C) and high pressures (up to 14 kg/cm^2) in the presence of two copper alloys.

Experimentals

The experimental apparatus consists of a steel reaction vessel, a membrane pressure gauge and high pressure valves which are set between the reaction vessel and an acetylene bomb or a vacuum pump respectively. The reaction vessel is 2 cm in inner diameter, 10 cm in inner length and 31.4 cc in capacity and is surrounded by an electric heater and heated to a given temperature. The temperature of the reaction vessel which is maintained within the accuracy of ±0.5°C is measured by means of two thermocouples which are inserted in the holes made in the wall of the reaction vessel. The membrane pressure gauge[5] is constructed by a spring steel

1) H. Erdmann and P. Koethner, *Z. anorg. Chem.*, **18**, 48 (1898)
2) A. E. Léger and E. Quellet, *Can. J. Res.*, **B28**, 358 (1950)
3) H. Kinoshita, *Unpublished*
4) R. Kiyama, J. Osugi and S. Kusuhara, *Unpublished*
5) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, **24**, 81 (1954)

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membrane (0.15 mm in thickness and 44 mm in effective diameter) and a mirror which rotates proportionally to the deflection of the membrane due to pressure changes. The pressure changes are measured from the displacement of a light spot reflected from the mirror on a scale which stands about 1.3 m distant from the mirror and the pressure sensitivity of the gauge is about 1 cm in the displacement of the light spot per 1 kg/cm^2.

Experimental procedures are as follows: the reaction vessel in which a clean copper alloy plate is set is evacuated and heated to a given temperature. Then acetylene gas is poured into the reaction vessel up to a given pressure and the valve is closed, and the reaction time is defined as zero at this instant. Thereafter the pressure changes of acetylene in the reaction vessel are measured at every definite time.

Acetylene gas is prepared with calcium carbide and water, purified through refining reagents, and compressed in a high pressure bomb up to 30~35 kg/cm^2. The purity of the acetylene gas used is 99.4~99.6%. The copper alloys used are commercial brass and phosphor bronze plates of 0.3 mm in thickness. They are cut in size of 4.9×1.8 cm, polished by a corundum cloth*, washed with methanol and then dried in air. The compositions of the alloys are as follows.

Brass	Cu	61%	Zn	39%	impurity	< 0.1%
Phosphor bronze	Cu	92~93%	Sn	6~7%	P	0.07~0.1%

Experimental Results and Considerations

In the experiment on newly polished and washed alloy, the induction period where the pressure hardly changes is observed. The rate of pressure decrease becomes higher with the lapse of time and then it shows the maximum value peculiar to the respective conditions and thereafter decreases gradually. The typical examples for the pressure changes under such conditions that the reaction temperature is 240°C and the initial pressure of acetylene is 13~14 kg/cm^2 are shown in Fig. 1.

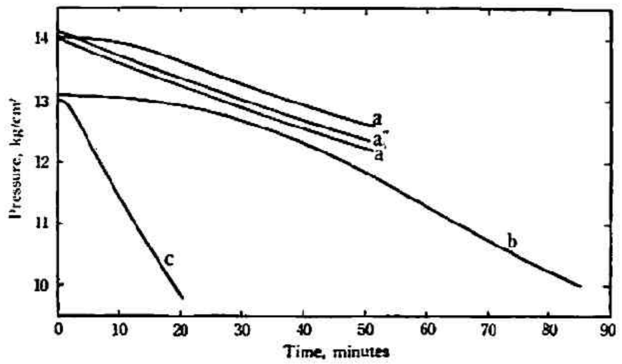

Fig. 1 Pressure-time curves of acetylene at 240°C in presence of newly polished copper or its alloys

a : brass
b : phosphor bronze
c : pure copper
a′, a″: brass used in the preceding runs

* Made by Minnesota Mining & MFG. Co., PT 31.

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In the case of brass (curve a), the maximum rate of pressure change is shown after the induction period of about 15 minutes, and in the case of phosphor bronze (curve b) the induction period extends over about more than 55 minutes. In contrast with those, in the presence of copper plate[4] (curve c) the maximum rate of the pressure change is observed in only 3 minutes after the start of the reaction. Generally speaking, for the same alloy, the induction period becomes shorter as the reaction temperature becomes higher, and becomes longer as the initial pressure of acetylene becomes lower. Curve a′ in Fig. 1 shows the run measured under the same conditions as those of curve a (brass, 240°). In curve a′ the reaction starts after evacuating the reaction gas in curve a for about 30 minutes and the maximum rate of pressure decrease is already observed at the start of the run (*cf.* Fig. 2 where it is shown clearly). Curve a″ shows the run measured again under the same conditions as those of curve a and a′ after several runs measured under various conditions using the same alloy plate. Curve a″ is in parallel with curve a′ and this fact means that the activity of the alloy does not vary with time or with the amount of product, and in other words, it is verified from these facts that the pressure-time curve has the reproducibility, being independent from the product. Therefore in present experiment,

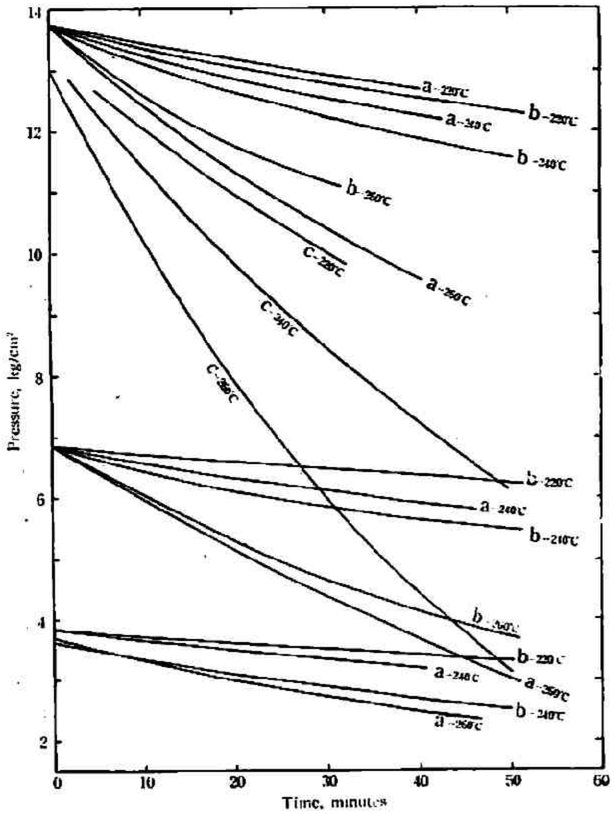

Fig. 2 Pressure-time curves of acetylene in presence of copper or its alloys which are not newly polished but used in the preceding runs

a: brass

b: phosphor bronze

c: pure copper

the measurements under various conditions with each alloy are performed continuously, not removing out the products but evacuating the reaction gas of the preceding run.

After the experiment, it was found that cuprene covers the surface of the alloy plate and adheres very slightly on the inner surface of the reaction vessel and on aluminium gaskets. Although it is shown from these facts that steel and aluminium have also some activities of catalyzing the cuprene formation, yet these activities are very weak as compared with copper or copper alloys. The polymerization of acetylene on the surface of the vessel and gaskets is neglected, since in blank test, the pressure changes due to the polymerization are scarcely observed under such conditions as those in the present experiment.

In the presence of brass or phosphor bronze which has been previously used in a few runs and has shown no induction period, the pressure changes of acetylene under various conditions of the initial pressure and temperature are shown in Fig. 2. In both cases of brass and phosphor bronze, the rate of pressure change increases with the temperature elevation, and at the same temperature, the rate decreases as the initial pressure decreases. Comparing both alloys under the same conditions, it is found that phosphor bronze is more active in acetylene polymerization than brass at 220° and 240°C, but at 260°C brass becomes more active than phosphor bronze. However, both alloys are much less active as compared with those of pure copper plate[4] (curves c), and the apparent rates of pressure changes with the alloys seem to be less than one half of those with copper plate.

As shown in Fig. 2, the rate of pressure change under each condition decreases with time and the pressure-time curve deviates from the straight line. From kinetic consideration, this would be due to the fact that zero order reaction and first order reaction would proceed in parallel, and in the initial period of the pressure change, the zero order reaction is thought to be predominant.[5] Therefore assuming that the rate of the reaction is zero order at the initial stage, the rate constant k_0 *i.e.* the derivative of pressure with time at the time of zero is evaluated from the curves and shown in the table. As described above, at 260°C the rate of pressure changes in the presence of brass is higher than that with phosphor bronze, but the values of k_0 show little difference in both cases. The activation energies E of the acetylene polymerization which are evaluated by plotting log k_0 against the reciprocal of absolute temperature are shown in the fifth column of the table. In the case of phosphor bronze, the activation energy decreases with the increase of the initial pressure, and the numerical values of the energies show good coincidence with those in the case of pure copper plate[4] (initial pressure 13 kg/cm^2—E=16.1 kcal, 7 kg/cm^2—18.3 kcal, and 4 kg/cm^2—20.3 kcal). On the contrary, however, in the case of brass the activation energy increases with the increase of the initial pressure.

The polymerization product (cuprene) on the surfaces of brass is yellow and that on the phosphor bronze is brown and they show neither explosive decomposition

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Table

Materials examined	Initial pressure of acetylene kg/cm²	Temperature °C	k_0 (per unit area)* mole/cc/sec	E kcal/mole
Brass	13.7	260	2.83×10^{-9}	29.5
	〃	240	0.959 〃	
	〃	220	0.691 〃	
	6.8	260	1.77 〃	27.6
	〃	240	0.643 〃	
	4.0	260	0.981 〃	24.0
	〃	240	0.406 〃	
Cuprene formed on brass	13.7	260	1.69 〃	30.7
	〃	240	0.548 〃	
Phosphor bronze	13.7	260	2.75 〃	16.7
	〃	240	1.29 〃	
	〃	220	0.759 〃	
	6.8	260	1.76 〃	18.4
	〃	240	0.904 〃	
	3.7	240	0.615 〃	19.2
	〃	220	0.287 〃	
Cuprene formed on phosphor bronze	13.7	260	1.22 〃	21.5
	〃	240	0.553 〃	

* The area of cuprene is assumed to be equal to that of alloy.

nor explosive combustion when heated in an atmosphere. The cuprene itself, when stripped off from the alloy plate, has also the activity for the polymerization of acetylene, and the pressure-time curves using the cuprene are compared in Fig. 3 with those using the alloy under the same conditions. The activity of cuprene varies in the qualitatively same manner as in the cases of the respective alloys on which it was produced. As described above, curves a, a′ and a″ in Fig. 1 which are performed under the same conditions show the same rate of pressure change, and it is clear from this fact that the activity of the alloy does not vary with the amount of the polymerization products on it. These would be ascribed to the fact that the cuprene

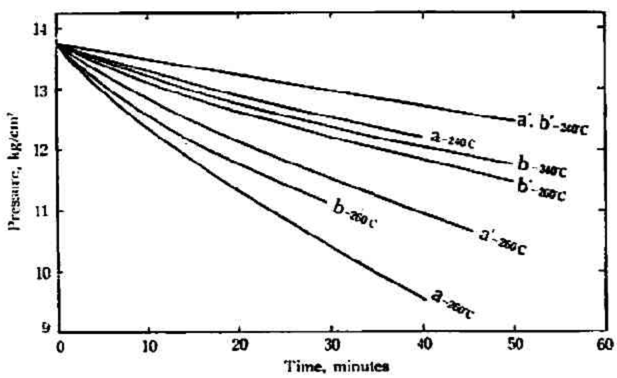

Fig. 3 Pressure-time curve of acetylene in presence of copper alloys or cuprene
a : brass
b : phosphor bronze
a′, b′: cuprene formed on brass or phosphor bronze respectively

produced on copper or copper alloys would include copper or cuprite in it[6] which would be active to polymerization of acetylene (growth of cuprene), and the amounts of the copper or the cuprite, depending on the alloy, would not vary even if the cuprene would grow. It would be considered, therefore, that the reaction rate would depend on the activity of the alloy itself even if the polymerization products, which themselves have some activity when stripped off from the alloy, would cover the surfaces of alloy and their amount would increase with the lapse of time.

Summarizing the results, copper and copper alloys show large activity on polymerization of acetylene under high temperatures, but when Zn, Sn, or P is added to copper, the activities of the resultant alloys are considerably decreased, and the addition of P seems to be especially influencial. In the cases of using alloys, the induction periods of the reaction become from several to several ten-folds longer than that in the case of copper, and from this point of view, the addition of P seems also especially influencial. The polymerization product itself has some activity when employed without the alloy, and its activity varies depending on the components of the alloy on which it was produced. The polymerization product shows no explosive nature and it is not considered that the presence of the polymer itself would take any part in the initiation of acetylene explosion.

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6) J. H. L. Watson, *J. Phys. & Colloid Chem.*, 54, 969 (1950)