## 11. Studies on the Swelling of Bentonite. (III)

*Sozaburo Ono* and *Takehiko Watanabe.*

The effects of autoclaving upon the degree of swelling of Japanese bentonites and their heat-treated samples were examined. The thermal dehydration curves of these samples were also obtained. Comparing these results with those of the preceding two reports (This Report, **17**, 101; **13**, 112 (1949)), the following conclusions were obtained.

1) By the autoclaving as well as the irradiation of ultrasonic waves, the bentonite, whose swelling has been markedly reduced in degree by heat-treatment, can be recovered in the degree of swelling. These effects may be attributed to the addition of a certain amount of water in some parts of the structure of bentonite whose decrease of swelling had been caused by the dehydration due to the previous heat-treatment.

2) The autoclaving exerts a favourable influence on the effect of the succeeding ultrasonic wave treatment.

3) The swelling capacity of bontonite may be due to the existence of some parts of bentonite where dehydration takes place in the two temperature ranges 450~800°C and 180~450°C. And the former determines whether the bentonite exhibits the swelling capacity or not.

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## 12. On the Reduction of Tungsten Oxide with Hydrogen (III)

### Reduction Velocity of Tungsten Oxide and Oxidation Velocity of Reduced Powder Measured by a Spring Balance.

*Nobuji Sasaki* and *Ryozo Ueda.*

The velecties of reduction of variously prepared pure tungsten oxides by flowing hydrogen at various temperatures and the velocities of oxidation of metallic powder thus formed by air at room temperature, were measured by means of a sensitive quartz fibre spring balance placed in the reaction tube. The higher the reduction temperature and the finer the oxide the more rapidly the trioxide could be reduced, but not below 400°C. Neither could the ammonium paratungstate be reduced at 400°C by hydrogen, but completely decomposed to trioxide without being reduced at all. The finer oxide (particle size: about $0.01\mu$) could be completely reduced to metal in 3 hrs. at as low as 480°C, while the coarse oxide (particle size: about $3\mu$) only to about 40% in 3 hrs. at 500°C. When reduced below 700°C, the products are liable to oxidation by air at room temperature. The velocity and extent of reoxidation are greater, if finer oxide and lower temperature of reduction are used. The product can even be pyrophoric. Primary particles or single crystal of tungsten produced by atomic sintering in the course of reduction of tungsten trioxide crystal with hydrogen, are necessarily small, if the reduction is carried out at lower temperatures, because the mobility of tungsten atoms or tungsten oxide molecules is then small. If again the trioxide crystals smaller than to form a single primary particle, the latter is naturally smaller than the ordinary primary particle. The presence of these smaller primary particles is the cause of the reoxidability of the tungsten powder. The spontaneous reoxidation of metallic tungsten powder at room temperature would be worth more attention in the tungsten powder metallurgy.

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## 13. On the "Precursory Recrystallization" in Copper Foils Prepared by the Mechanical Rolling.

*Hideki Hirata, Masashige Koyama* and *Katsuyuki Yasuda.*

A peculiar phenomenon as may be called a "Precursory Recrystallization", which had been found in our foregoing investigation with iron and nickel, pulverized (Rev. Phys. Chem. Japan, Commemoration Vol. 86 (1946)), or rolled (Rep. Inst. Chem. Research, Kyoto Univ., 18, 94 (1914)) mechanically, was inferred to occur in the most metals affected by some severe inner strain. To make it clear whether such an inference were correct or not, the progress of the structural change due to the various procedures of annealing of some copper foil (reduction percentages in thickness amount to 62.7%~99.89%) was examined with X-rays similarly as in the previous experiments.

As the consequence of the present X-ray examination, it was confirmed that the usual recrystallization phenomenon in all the copper foils examined, takes place at a temperature 100°C~250°C, irrespectively of the duration of annealing (2 min.~5 hr.); i. e., at the temperature above stated, the growth of micro-crystals forming these foils, which had arranged themselves in a fibrous way, was observed to take place, together with the conversion of the fibrous from $\langle 111 \rangle$ axis to $\langle 100 \rangle$ axis parallel to the direction of rolling.

Among these foils, those corresponding to the reduction percentages 97.31%~99.68% were especially noticed to give rise to the "P. R." at a temperature 50°C~120°C. By this "P. R.", two fibrous arrangements, each having $\langle 111 \rangle$ axis of the micro-crystals in common, were seen to be newly formed. One of these had its common axis parallel fo the direction of rolling; while in the other, its common axis was seen to be situated normal to the aforesaid direction. Here, it must be remarked that such a structural change due to the "P. R." was also observed to be