A Microphotographic Research on Salt System: $NaNO_2$—KNO_3

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Introduction

A considerable amount of microphotographic study on the metallic alloys has been made with the aid of a metallographic microscope, but little has been made on the salt systems. The reason seems to lie in some difficulties of observing directly the state of the etched surface of the salt ingot under the metallographic microscope, because its etched surface is liable to glitter dazzlingly all over the sample. W. M. Magden[1], S. F. Žemczužny[2], E. Shibata & H. Imai[3], A. Kofler[4] have reported microscopical technique of investigating binary salt systems, chiefly for the case of eutectics. But they were not successful in observing the microscopic structures of specimens in the case of solid solution except the silicates and the unhygroscopic salts because of some technical difficulties.

As the $NaNO_2$-KNO_3 system contains the hygroscopic salt ($NaNO_2$), the surfaces of etched specimens become stained during the process of polishing. Besides the specimens of this system are fragile and porous, therefore it is doubtful whether this system belongs to the solid solution type or to the eutectic type. If this system belongs to the former, the dendrite crystals of soild solution can not be observed microscopically by the usual technique, because they are not composed of pure salt like those in the eutectic case. So the author intended to improve the technique and succeeded in taking a clear microphotograph of this system.

Experimental

(1) Thermal Analysis and Electric Conductivity Measurement.—Kagan and Kamuischan[5] made the thermal analysis of the $NaNO_2$-KNO_3 system and found it to be a case of solid solution (It was found somewhat round in the neighbourhood of the temperature minimum 141.1°C, 46 5 Mol.% KNO_3); but it is not so sure unless the microscopical observations are made, because the heat capacities of the specimens are extremely small and the obtained cooling curves are so irregular that it is doubtful whether this system belongs to the solid solution type or to the eutectic type.

The author made a study on phase diagram of this system by means of thermal analysis and electric conductivity measurement by using an electric furnace of sufficiently large heat capacity. The cooling rate was ca. 1°C./45 sec. between 200–300°C., the same as in the research of Kasé[6]. Fig. 1 shows the results obtained. But the author failed to determine the accurate liquidus by these two methods alone because the cooling curves are of very slow slope.

Fig. 1 also shows that the solidus obtained by conductivity method* always lies under that of thermal data. Because in the practice of thermal

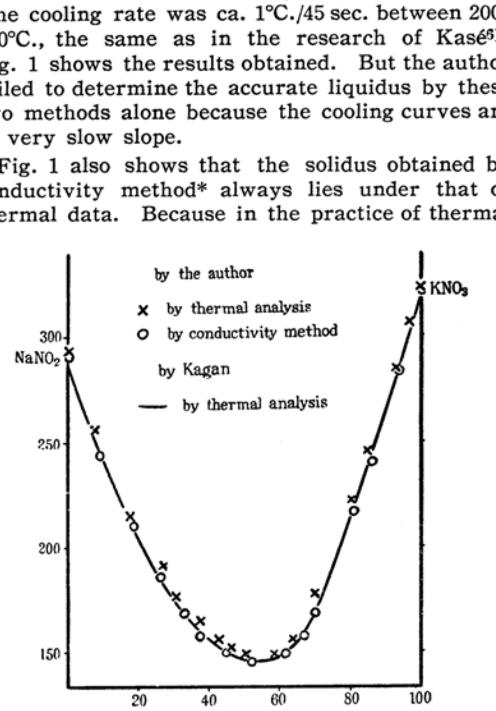

Fig. 1. Phase diagram of $NaNO_2$—KNO_3

1) W. M. Magden, *J. Chem. Soc.*, 458 (1930), 874 (1930).
2) S. F. Žemczužny, *Z. anorg. Chem.*, **153**, 47 (1926).
3) E. Shibata, H. Imai, *J. Sci. Hiroshima Univ.* A**14**, 1 (1949).
4) A. Kofler, *Chem. Ber.*, **85**, 447 (1952).
5) M. Ya. Kagan and N. Kamuischan, *J. Applied Chem.* (U. S. S. R.) 5347 (1932); *Chem. Abstr.*, **27**, 15 (1933).
6) T. Kasé, *J. Applied Phys. Japan*, **7**, 213 (1938).
* The used apparatus is the same as that described in *J. Chem. Soc.* (Japan) Pure Chem. Sec. **75**, 64 (1954).

analysis the thermocouple is set in the centre of the melt, we cannot get rid of the thermal effect occuring from the segregation, but in the case of the electric conductivity there is little error from that source.

(2) Microscopic Method

(*a*) *Method of flattening the surfaces of salt ingots*.—To smooth the surfaces of ingots, it is usually necessary to polish them with the various grades of emery papers and the soft brushes made of flannel. But the ingots of this system are so fragile and porous that their surfaces are liable to be damaged during the process of polishing, and the more they include large amount of KNO_3, the more fragile and porous they become. So the following method is recommended. Mixes of $NaNO_2$ and KNO_3 in various proportions are prepared in a quartz crucible (Fig. 2) which is composed

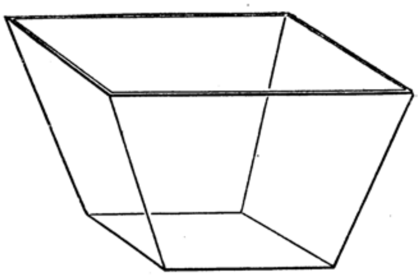

Fig. 2. Quartz crucible.

of five well-polished quartz plates. By the help of this crucible, we are now able to avoid all the troubles in cutting and polishing the surfaces of ingots, because the five surfaces of ingot facing the crucible plates are already as glassy as mirrors.

(*b*) *Method of etching*.—The surfaces of the obtained specimens are etched with etching solution. In this case the author used the saturated KNO_3 solution in 25% alcohol*, because in etching the surfaces of specimens it is recommended to use the saturated solution of the salt of smaller solubility of the two.

(*c*) *Microscopic operation*.—After the above treatment the etched surfaces are pressed on celluloid plates, slightly moistened with amylacetate in which a small amount of celluloid is dissolved. A few minutes later, the celluloid plates are carefully peeled off and examined microscopically.

When the quartz crucible does not react with salt ingot, we have now become able to study phase diagrams of almost all salt systems as easily as those of metallic alloy. Thus, the microphotographic method of studying salt systems can be applied not only to the unhygroscopic specimens but also to the hygroscopic, fragile and porous specimens such as mentioned above.

* E. Shibata used water as the solvent, but it is inadequate because of its high solubility.

Results and Discussions

The dendrite crystals of solid solution are found in the above inserted Photo. 1–5. The shapes of dendrite crystals closely resemble those of Cu-Ni[7,8], Cu-Sn[9] alloys, steel[10] and devitrified glass[11]. The dendrite structure of solid solution occurs in the state of imperfect equilibrium, and when the cooling rate is comparatively rapid, the diffusion of each ion of the mixed salts may be interrupted. So, if the specimens are annealed at the neighborhood of melting points, each ion of salts may diffuse slowly, and the concentration at each part of the melt may become uniform; then the dendrite crystals of soild solution may entirely disappear. See Photo. 6. If the $NaNO_2$—KNO_3 system belongs to a eutectic without any solid solution range, dendrite crystals should not disappear, and moreover, the areas occupied by dendrite crystals in the whole area ought to be varied as the composition changes. But it has been found out by this experiment that the areas of dendrite crystals are always constant on the whole. See Photos. 1–5. This fact also shows that this system belongs to a case of solid solution. And if the cooling rate can be limited within the proper extent to give rise to dendrite crystal, the size of dendrite may become maximum, when the cooling rate is minimum. It is proved by Photos. 1, 3, 4 and 5.

Summary

(1) The phase diagram of the $NaNO_2$–KNO_3 system was constructed by the thermal analysis and the electric conductivity measurements. The solidus on the whole is the same as found by Kagan.

(2) By the microphotographic method it was ascertained that this system belongs to a case of soild solution just as Kagan had inferred and that the nature of dendrite crystals in solid solution of the salts closely resembles those of alloys and devitrified glass.

(2) By the improved technique the microphotographic method of studying salt systems has now become able to apply to almost all salt systems.

7) I. Iitaka, *Bull. Inst. Phys. Chem. Res.* **13**, 1395 (1934).
8) S. H. Carpenter, J. M. Robertson, *Metals*, **1**, 223 (1939).
9) A. Sauveur, *Trans. Amer. Soc. for Steel Treating*, July, I (1923).
10) A. Sauveur, "Metallography and Heat Treatment of Iron and Steel", Chap. 3 (1933).
11) J. Sugie, Study of 'Glass Crystals', 8 (1943).

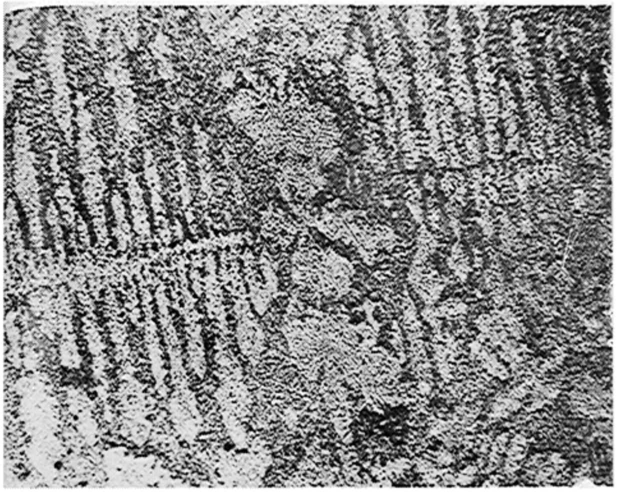

Photo. 1
×80, 24 wt. % KNO_3 (Rapid Cooling)

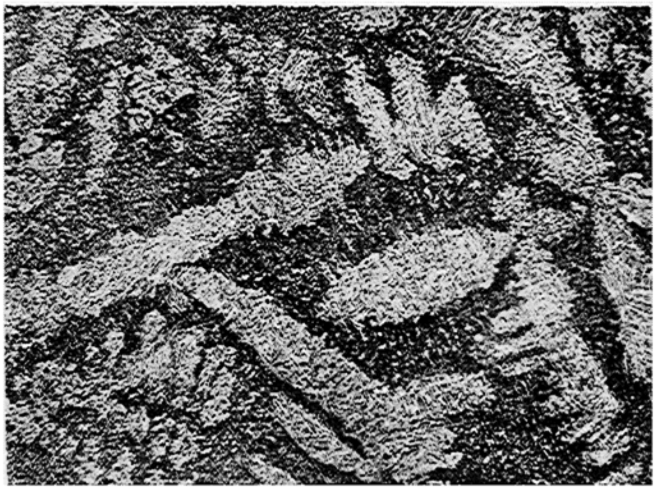

Photo. 2
×80, 34 wt. % KNO_3 (Medium Cooling)

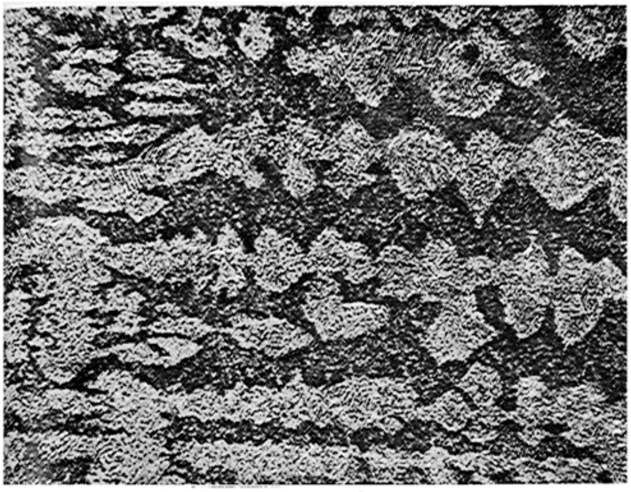

Photo. 3
×75, 51.5 wt. % KNO_3 (Slow Cooling)

Photo. 4
×75, 65 wt. % KNO_3 (Slow Cooling)

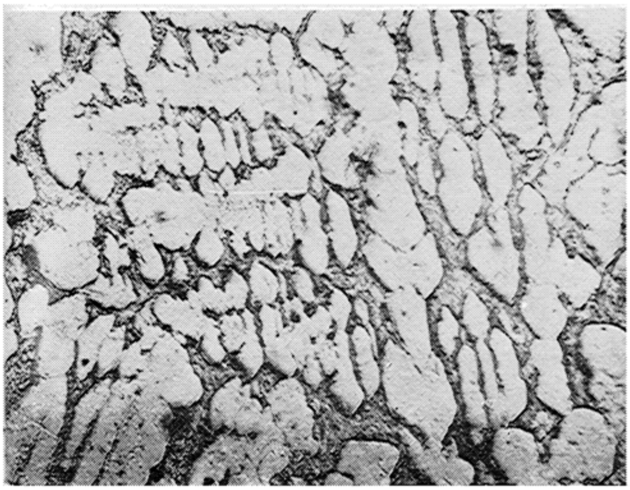

Photo. 5
×75, 82 wt. % KNO_3 (Slow Cooling)

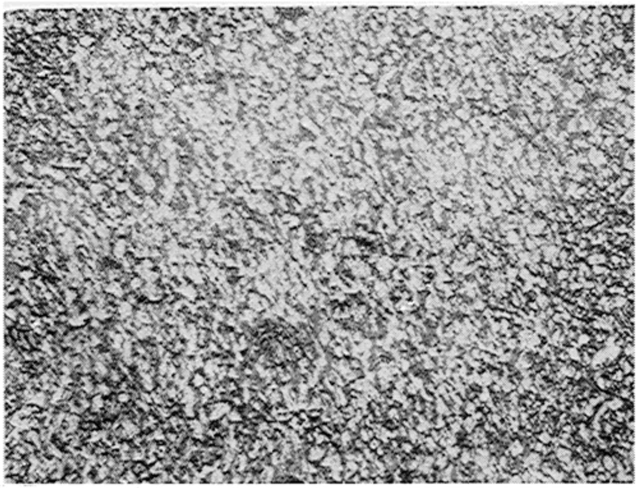

Photo. 6
×80, 82 wt. % KNO_3 (Annealed)

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