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DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF THE SOLID–SOLID TRANSITIONS IN $NaNO_2$-BASE BINARY ALLOYS WITH $NaNO_3$ AND KNO_2

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ABSTRACT

Up to ~1 mol % maximum solid solubility of KNO_2 or $NaNO_3$, the two solid–solid transition temperatures in $NaNO_2$-base alloys decrease ~11 ± 4 deg per mol % solute, except that the upper transition temperature is hardly altered by alloying with KNO_2. From the data on alloys with KNO_2, the ratio of the entropy of the upper transition to the lower transition in $NaNO_2$ is estimated as 0.35 ± 0.07.

For $NaNO_2$, there are two very thoroughly investigated[1–8] solid–solid phase transitions occurring quite close together in temperature. One at the lower temperature ("lower transition") being first-order but with rapid variations in specific heat, thermal expansions, etc. ("λ-like") near the transition temperature and the other ("upper transition") being entirely λ-like and without any first-order component. This investigation aimed at determining the variations of the transition temperatures with alloying in two particular terminal solid solutions and has also yielded more insight into the problem of the entropies associated with each transition, which are not obvious from the specific heat data[4–7] for pure $NaNO_2$ because of the overlapping λ-like peaks. Solutes were chosen in which only one ion was replaced in $NaNO_2$ and that by an ion not only similar in charge but also in size so that more extensive solid solubility is favored. Gesi[8] has already shown, by DTA, that the lower transition temperature is increased more by alloying with $AgNO_2$ than the upper transition temperature such that the two transitions merge into one at ~1 mol% $AgNO_2$. The present work shows that alloying with $NaNO_3$ decreases the upper transition temperature at least as much as the lower transition temperature so that the transitions cannot be distinguished whereas alloying with KNO_2 scarcely alters the upper transition temperature but decreases the lower transition temperature such that the two are more nearly distinguishable.

Merck reagent $NaNO_2$ and $NaNO_3$ and Baker's analyzed (94%) KNO_2 were dried under at least 10^{-2} torr for several hours near 120°C. In the alloy preparation,

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which was similar to previous work[9,10] the molten alloys were quenched rapidly, after homogenization, into thin layers in a porcelain dish so as to retain metastable solid solutions[11]. Standard sample capsules were used with the Perkin-Elmer DSC-1B, with sample preparation and an empty capsule for reference, as before[9,10]. Calibrations were made at room temperature, with the melting points of the standard indium and tin samples and with the λ transition in $NaNO_3$ (ref. 9). $NaNO_2$ samples were also run occasionally to enhance precision. Thus, temperatures are believed accurate to probably ± 1 °C. Precision and reproducibility in the experiments appeared to be of the order of ± 1 °C.

Samples of different masses and compositions were heated and cooled at rates of 4, 8, 16, 32 and 64 deg min^{-1}. Transition temperatures were taken as the maxima in the thermal effects. Linear plots of transition temperatures vs. rate, for the heating and cooling data, respectively, yielded the transition temperatures at zero rate by linear extrapolation. The proportionality factor was 0.22±0.03 deg per deg min^{-1} and

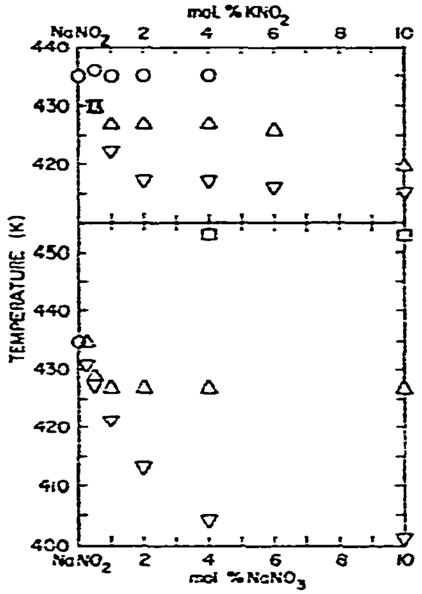

Fig. 1. Transition temperatures at zero heating/cooling rate for various $NaNO_2$–KNO_2 (upper portion) and $NaNO_2$–$NaNO_3$ (lower portion) alloys. ○, upper transition temperatures obtained on both heating and cooling; □, transition temperatures in concentrated $NaNO_2$–$NaNO_3$ alloys observed only on heating; △, lower transition temperatures obtained on heating and on cooling, those from heating lying at higher temperature for a given alloy.

symmetric for heating and cooling, except for these alloys which showed appreciable temperature differences between the transitions on heating and on cooling; these results are consonant with previous experience[9,10]. Transition temperatures at zero rate are shown in Fig. 1 for both the $NaNO_3$ and KNO_2 alloys.

The thermal cycles finally used were: heat initially from room temperature to 460 K (for the KNO_2 alloys) or 480 K (for the $NaNO_3$ alloys) at 16 deg min^{-1} which yielded the transition for the metastable* solid solution in the rapidly quenched samples; anneal so as to obtain reproducible, time-independent results ("equilibrate") at 460 K or 480 K for 30 min; heat and cool at the other rates for the range 330–360 K to 460 K or 480 K; heat over this range at 16 deg min^{-1} again, to verify reproducibility. For pure $NaNO_2$, the peaks corresponding to the two transitions could not be resolved effectively with this DSC; at the lower rates, the upper peak could be seen as a bump on the flank of the larger lower peak though. For the $NaNO_2$–$NaNO_3$ alloys, only a single peak was observed and, for alloys containing $\geqslant 4$ mol % $NaNO_3$, another transition was observed at ~453 K on heating only.

For the $NaNO_2$–KNO_2 alloys, the peaks were increasingly separated in temperature with alloying, which decreases the lower transition temperature (Fig. 1). The upper peak remained fairly acute upon alloying whereas the lower peak broadened considerably. Areas under peaks corresponding to the two phase transitions were determined by counting squares on the chart paper. For the same sensitivity, chart speed and slope adjustment of the DSC, acceptable linear "baselines" could be drawn from temperatures of 330–360 K, well below the transitions, to the maximum temperature of 460 K used here, for rates of 4,8 and 16 deg min^{-1}. For higher rates, acceptable baselines could not be drawn; for lower rates, the noise was too great. Acceptable baselines could not be drawn for the cooling curves (for the particular slope adjustments used) and hence all areal data are from the heating curves. For both sets of alloys, a linear correlation to within ~10% was found between sample mass (over range of 10–32 mg) and area of the initial peak (before equilibrium) at 16 deg min^{-1}. However, more precise comparisons could be made between peak areas for a given sample rather than between samples. From eight different runs with $NaNO_2$–KNO_2 alloys, the total areas under the peaks, after equilibration, were 0.91 ± 0.03 times the areas under the initial peak, before equilibration, at 16 deg min^{-1} on heating.

For the $NaNO_2$–KNO_2 alloys, the division between the areas corresponding to the lower and upper peaks was made at the temperature corresponding to the minimum in the valley between the peaks. This division seems justified by the consistent data from the dilute alloys where the difference between transition temperatures varies. Plotted in Fig. 2 are the areas under the upper transition peak vs. the areas under the lower transition peak for various samples heated at rates of 4, 8 and 16 deg min^{-1}. The data for the 1/2 and 1 mol % KNO_2–$NaNO_2$ alloys essentially coincide (Fig. 2) and the ratio area (upper transition):area (lower transition) $= 0.35 \pm 0.07$. Of the several sets[4–7] of specific heat data for pure $NaNO_2$, the most extensive[6] from Sakiyama et al. suggest entropy (upper transition): entropy (lower transition) $\approx 0.22/1.04 \approx 0.21$, where the temperature corresponding to the bottom of the valley is within $\lesssim 1°$ of the peak temperatures.

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*Investigations could not be continued for these metastable phases because they tended to decompose toward equilibrium after a couple of heating and cooling cycles through the transition.

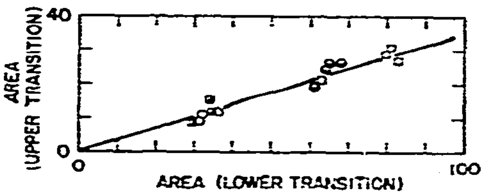

Fig. 2. Plot, in arbitrary units, of areas under the upper transition peak vs. areas under the lower transition peak ½(○ ●) and 1(□ ■) mol % KNO_2–$NaNO_2$ alloys at heating rates of 4, 8 and 16 deg min^{-1}. (The different heating rates are not indicated and there is no systematic correlation with the deviations from the fit.) The drawn line corresponds to a slope of 0.35 and an uncertainty of ±0.07 will include all of the data.

From the fragmentary data obtainable before equilibration, it seems that there is hardly any variation of transition temperature in the metastable solid solutions with both $NaNO_3$ and KNO_2. For the $NaNO_2$–KNO_2 alloys near equilibrium (Fig. 1), the upper transition temperature is virtually unaffected by alloying whereas the lower transition temperature decreases $\sim 11 \pm 4$ deg per mol % KNO_2, with a solubility limit of ~ 1 mol % KNO_2. The broadening of the lower transition and considerable difference ("hysteresis") between transition temperatures on heating and cooling are compatible with that transition having a first-order component whereas the negligible hysteresis for the upper transition suggests that it remains entirely λ-like. Data[12] for the equilibrium phase relations in the $NaNO_2$–KNO_2 system are fragmentary but seem reasonably consistent with the present results.

For the $NaNO_2$–$NaNO_3$ alloys near equilibrium (Fig. 1), the lower transition temperature decreases $\sim 11 \pm 4$ deg per mol % $NaNO_3$, with a solubility limit of ~ 1 mol % $NaNO_3$ and the transition also broadens with alloying. The trajectory of the upper transition is not known but is constrained to decrease in temperature at least as steeply as the lower transition does. The equilibrium phase relations for the $NaNO_2$–$NaNO_3$ system reported by Bergman et al.[13] appear consistent with the present results and also for the transition detected near 453 K in the concentrated alloys, although there are minor differences in transition temperatures.

With respect to microscopic models[14] for $NaNO_2$, the alloy results may possibly be interpreted as follows. Replacement of polar NO_2^- ions by non-polar NO_3^- ions reduces the stability of the lower temperature (ferroelectric and antiferroelectric) phases. Replacements of Na^+ ions by the larger Ag^+ and K^+ ions have differing effects on the relative stabilities of the three phases. Probably important here is the higher polarizability[15] of the Ag^+ ion as compared to the K^+ ion, both being considerably larger than the polarizability of the Na^+ ion.

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