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STUDIES ON PARAMETERS CONTROLLING THE DEGREE OF UNDERCOOLING, NAPHTHALENE–PICRIC ACID AND ANTHRACENE–PICRIC ACID SYSTEMS

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ABSTRACT

The effects of cooling cycle number, cooling rate, quantity of melt and alloy composition on degree of undercooling were determined experimentally. Naphthalene–picric acid and anthracene–picric acid were chosen for the detailed studies. The intensity of the effect on the two systems was different but the trend was the same. The undercooling, instead of being a definite value, was found to be a function of cooling rate, melt quantity, alloy composition and the freezing cycle number.

INTRODUCTION

In a number of investigations [1–6] into the undercooling of bulk samples of liquid melts, where the undercooling temperature is determined from the arrest or reversal point on the continuous cooling curves, the effect of variants such as the cooling rate, freezing cycle number, quantity of melt, and the alloy composition have not been adequately accounted for or have been totally ignored. For an arrest or reversal of a cooling curve to occur, the instantaneous rate of release of the heat of transformation corresponding to mixing and solidification must exceed the instantaneous rate of heat withdrawal resulting from the imposed temperature gradients. Moreover, the effect of repeated heating and cooling on the number of nucleants responsible for starting the process of solidification and the effect of solute concentration on growth rate are such significant factors that they would not leave the degree of undercooling unchanged.

In the present work the effect of these parameters on the degree of undercooling of pure naphthalene, anthracene, picric acid, eutectics and the

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complexes of naphthalene–picric acid and anthracene–picric acid has been studied.

EXPERIMENTAL

Materials and purification

The parent components, namely naphthalene, anthracene and picric acid, were from BDH, Analar, Bombay, which were further purified by fractional crystallization and sublimation. Naphthalene was purified by sublimation, followed by recrystallization from cyclohexane in a sealed tube. Anthracene was recrystallized twice in succession from ethanol and benzene. Picric acid was purified by fractional crystallization from ethanol. The purity was confirmed by melting point measurements. The melting points of naphthalene, anthracene and picric acid were 80.2, 216.3 and 122.5°C, respectively. These values are in good agreement with the literature values [7].

Techniques

The composition of eutectics and that of the complex was determined by the phase-diagram method and undercooling data were obtained for pure naphthalene, anthracene, picric acid, eutectics and the complexes by usual techniques [8,9]. Pyrex glass bulbs jointed with a 15 cm long, 10 mm OD tube were used as sample holders for the nucleation studies. The sizes of the bulbs were chosen according to the sample mass. The bulbs were cleaned with organic solvents followed by chromic acid. Sulphuric acid was left in the bulb for 24 h. Finally, the bulbs were washed several times with distilled water and dried in an oven maintained at 150°C. A nichrome-wire heater (25 ohms) was built on the tube, 10 cm from the neck of the bulb. After filling the bulb with a weighed amount of the sample, the bulb was placed in an oil bath which was maintained approximately 30°C above the melting temperature of the sample. The heater was energized to prevent any nucleation from the top of the bulb. After 10–15 min, the bulb was placed in a cooling bath to determine the undercoolings. At the maximum undercooling, nucleation always started from the bottom of the bulb. The rate of cooling was controlled by the relative variation of rate of heating and the radiation rate of the sample to the surroundings. The degree of undercooling of pure components, eutectics and that of the complex were determined at various cooling rates, with the different quantities of the melt and after a number of times of heating and cooling of the system.

RESULTS AND DISCUSSION

The undercooling results are presented in Tables 1 and 2. The cooling rate varies with the pure sample or the type of alloy. Since cooling is mainly

TABLE 1

Effect of rate of cooling, freezing cycle number and quantity of melt on undercooling of the systems

Sample	Rate of cooling (°C min^{-1})	Under-cooling, ΔT (°C)	No. of cycles, n	Under-cooling, ΔT (°C)	Quantity (g)	Under-cooling, ΔT (°C)
Set A						
(I) Anthracene	1.4	4.2	2	7.3	1.5	4.8
	5.0	7.1	3	9.4	10.8	7.2
	8.5	10.2	4	11.6	20.4	10.4
	12.2	13.6	5	13.8	25.1	13.5
(II) Picric acid	5.8	8.5	2	10.2	3.0	9.6
	9.5	12.5	3	12.5	15.5	7.2
	11.4	14.5	4	15.2	21.5	6.3
	12.5	16.0	5	15.5	25.6	5.7
			6	15.5		
(III) Anthracene–picric acid eutectic-1	1.5	5.6	2	2.2	5.2	9.3
	3.0	7.0	5	9.5	8.2	11.4
	7.3	11.2	6	12.0	10.6	12.5
	11.8	14.8	7	14.4	14.8	13.6
			8	14.4		
			9	14.4		
(IV) Anthracene–picric acid eutectic-2	2.0	7.1	2	2.8	4.8	11.0
	4.5	9.4	5	10.2	10.5	12.6
	8.0	12.8	6	12.6	15.2	13.8
	12.8	16.3	7	15.1	20.8	15.2
			8	15.1		
			9	15.1		
(V) Anthracene–picric acid complex	1.8	6.8	2	3.8	3.7	9.8
	5.2	9.7	5	6.1	8.2	12.1
	8.8	12.8	6	8.7	10.3	14.4
	12.3	16.0	7	11.4	15.4	16.5
			8	16.2		
			9	16.2		
Set B						
(I) Naphthalene	1.6	1.1	2	10	2.5	10.2
	4.6	5.5	3	10.5	10.5	9.8
	7.6	10.5	4	11.5	15.0	8.2
	9.2	12.0	5	11.5	20.8	6.0
			6	11.5		
(II) Naphthalene–picric acid eutectic-1	3.3	6.5	2	5.8	1.5	8.1
	8.2	10.0	4	10.2	5.2	6.8
	12.6	14.5	5	12.8	10.6	4.9
	13.0	15.0	6	13.2	15.7	2.8
			7	13.2		
			8	13.2		

TABLE 1 (continued)

Sample	Rate of cooling (°C min^{-1})	Under-cooling, ΔT (°C)	No. of cycles, n	Under-cooling, ΔT (°C)	Quantity (g)	Under-cooling, ΔT (°C)
(III) Naphthalene–picric acid eutectic-2	4.6	5.0	2	9.4	1.0	10.6
	8.5	12.0	4	13.5	4.5	8.2
	10.6	15.0	5	16.0	8.6	6.4
	12.7	16.5	6	16.5	12.5	4.3
			7	16.5		
			8	16.5		
(IV) Naphthalene–picric acid complex	5.5	10.0	2	5.0	1.2	11.6
	8.4	13.0	4	12.5	3.8	9.2
	10.5	16.0	5	16.0	7.2	7.3
	13.1	18.0	6	17.2	12.3	6.2

radiative, the higher-melting point compounds have significantly higher cooling rates than the lower-melting ones. The results show that in all cases undercooling is significantly greater (Figs. 1 and 2) at the faster cooling rate. The arrest or reversal of cooling rate requires the instantaneous rate of release of heat of transformation to exceed the instantaneous heat-withdrawal rate resulting from the imposed temperature gradients. It is clear that the instantaneous rate of release of heat of transformation (essentially due to solidification) is determined by the nucleation and the liquid → solid volume transformation rates. In the simplest case, assuming spherical growth and a constant radial growth rate, the volume rate of growth of a crystal increases with the square of the radius or the time, and as such is mainly time-determined and only slightly affected by the cooling rate. If the nucleation rate is not sufficiently increased with increased cooling rate, then the liquid–solid mixture will supercool to a lower temperature before the transformation rate with its corresponding rate of evolution of heat, eventually equalizes or even surfaces the rate of heat withdrawal.

TABLE 2

Effect of alloy composition on undercooling

Mole fraction of naphthalene in picric acid	Undercooling, ΔT (°C)	Mole fraction of anthracene in picric acid	Undercooling, ΔT (°C)
0.0000	15.3	0.0000	15.3
0.2132 (E-1)	13.0	0.1017 (E-1)	14.5
0.9405 (E-2)	16.5	0.6250 (E-2)	16.1
1.0000	11.2	1.0000	13.5

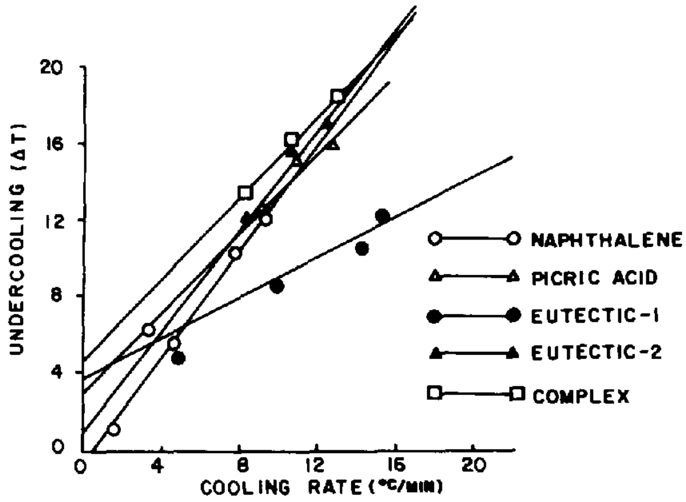

Fig. 1. Effect of cooling rate on undercooling of the naphthalene–picric acid system.

Generally, the maximum degree of undercooling achieved in the melt depends upon the number of freezing cycles used. Initially the melt nucleated only after few degrees below the equilibrium liquidus temperature, while on repeated melting and freezing, a reproducible undercooling could be achieved after 4–6 cycles (Figs. 3 and 4). The saturation cycle number for the pure components was found to be smaller than those for the eutectics and the complex. This can be explained such that the nucleants are responsible for starting solidification and every cycle removes a fraction of total nucleants enabling the melt to undergo solidification progressively at a lower tempera-

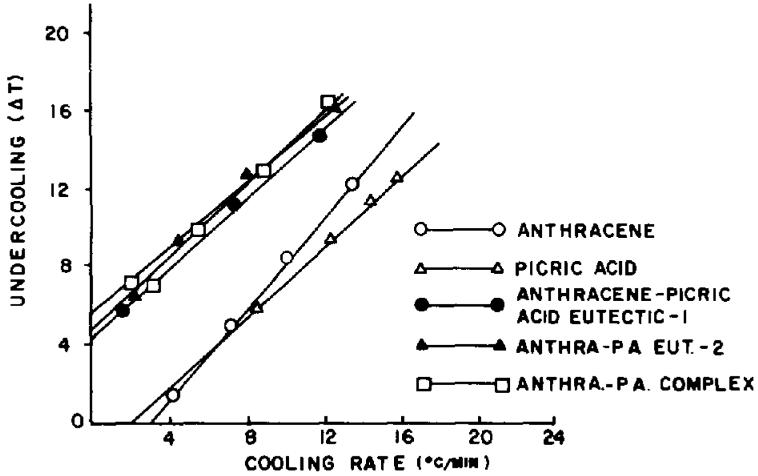

Fig. 2. Effect of cooling rate on undercooling of the anthracene–picric acid system.

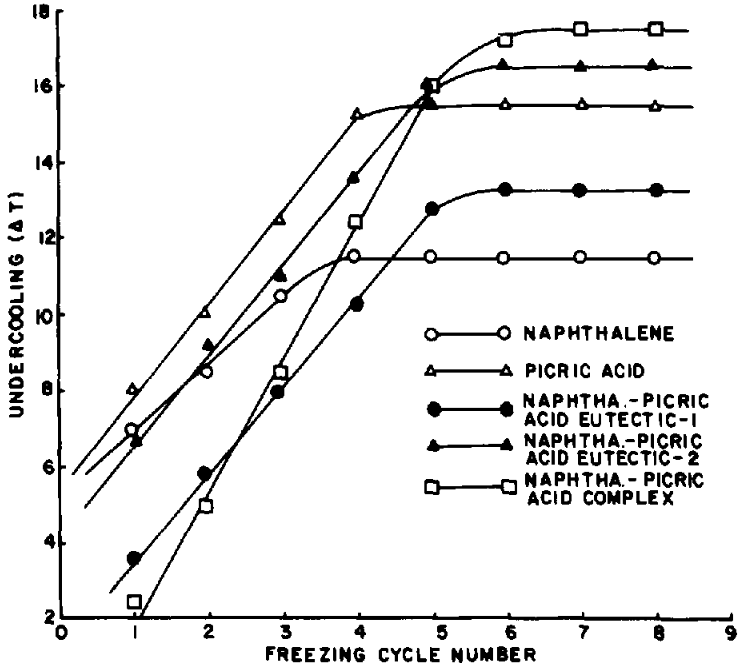

Fig. 3. Effect of freezing cycle number on degree of undercooling of the naphthalene–picric acid system.

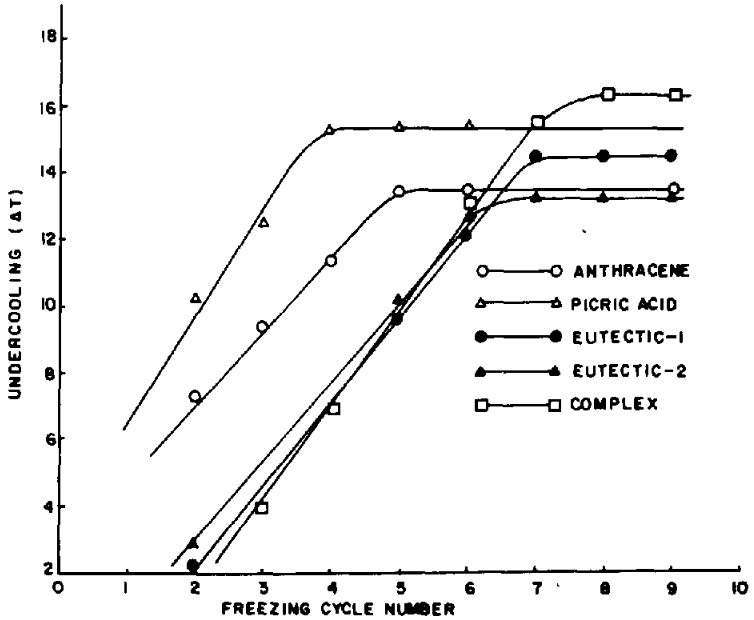

Fig. 4. Effect of freezing cycle number on degree of undercooling of the anthracene–picric acid system.

ture with the increasing cycle number. A consistent undercooling is achieved when all the nucleants are removed in this way. The removal of nucleants in the case of pure components seems to be easier than those of the eutectics and the complex.

The maximum degrees of undercooling and recoalescences attained in naphthalene–picric acid and anthracene–picric acid melts were observed to vary with the total quantity of the sample (Table 1). In an earlier investigation Ohashi et al. [10] observed a similar dependence of undercooling on the quantity of melts. Kattamis and Flemings [11] argued that a simple thermal balance between the rate of evolution of latent heat of fusion and rate of loss of heat to the surroundings can be used to show that in a bulk melt recoalescence is sufficient to bring the temperature of the melt to its equilibrium freezing point. When the melt is in a small quantity, the available latent heat may not be sufficient to raise the temperature of the undercooled liquid to the equilibrium freezing point, possibly due to faster conduction and loss of heat to the surroundings. Additionally, the higher undercooling of a smaller quantity of melt may also be due to the relatively lower number of nucleants present as compared to the bulk melt.

Youdelis and Iyer [12] have recently reported the effect of alloy composition on the degree of undercooling in several binary alloys systems. In our system it was observed that the undercooling increases as the composition of the alloy approaches the eutectic composition. Our experimental observation can explain the growth rate of primary crystals, which primarily depends on the rate of diffusion of solvent atoms to the crystal–liquid interface, decreases with increasing solute concentration. The decreased crystal growth rate resulted in a correspondingly lower rate of heat evolution so that the melt undercooled to a greater degree.

CONCLUSION

The undercooling temperature for a bulk sample, as determined from the cooling curve, cannot be taken as the temperature at which the nucleation is initiated, but is an arbitrary value which is a function of cooling rate, quantity of melt, freezing cycle number and the alloy composition. The effect of these parameters on the degree of undercooling was qualitatively alike but differed quantitatively in the case of these systems.

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REFERENCES

1 G.L.F. Powell and G.A. Colligan, J. Inst. Met. 97 (1969) 319.
2 G.L.F. Powell and G.A. Colligan, Trans. Metall. Soc. AIME, 245 (1969) 1913.
3 J.T. Jubbs and W.C. Winegard, Can. Metall. Q., 4(2) (1965) 145.
4 R.P. Rastogi and Ram Gopal, J. Indian Chem. Soc., 27 (1950) 403.
5 N.P. Singh, R.N. Singh, O.P. Singh and N.B. Singh, Krist. Tech., 14 (1979) 6.
6 N.B. Singh and K.D. Dwivedi, J. Sci. Ind. Res., (1982) 677.
7 Lange's Hand Book of Chemistry, McGraw-Hill, New York, 1982, p. 98.
8 R.P. Rastogi and P.S. Bassi, J. Phys. Chem., 68 (1964) 2398.
9 S.N. Ojha, Ph.D. Thesis, Varanasi, India, 1973.
10 T. Ohasi, H. Fuju, Y. Nuri and K. Anano, Trans. Iron Steel Inst., Jpn., 17 (1977) 262.
11 T.Z.Kattamis and M.C. Flemings, Mod. Cast., 52 (1967) 67.
12 W.V. Youdelis and S.D. Iyer, J. Inst. Met., 101 (1973) 176.