PHASE SEPARATION IN TRANSPARENT LIQUID-LIQUID MISCIBILITY GAP SYSTEMS

by

S. H. Gelles, B. N. Bhat[(a)] and R. J. Laub[(b)]

INTRODUCTION

The field of processing materials in space has provided a renewed incentive to study materials systems containing a liquid phase miscibility gap, i.e., a field in the phase diagram representing the equilibrium between two liquid phases. These studies have concentrated on understanding the development of both the macro- and microstructures of these materials during thermal processing and have also taken advantage of the low-gravity environment afforded by sounding rockets and orbiting spacecraft to minimize the effects of buoyancy and fluid flow. The programs have generally concentrated on <u>opaque</u> metallic systems and have been primarily concerned with the separation process wherein a single phase liquid transforms into two liquid phases and with the accompanying coalescence processes. Since solidification can affect the macro- and microstructures, this transformation has been studied as well.

As will be delineated in what follows, the studies of the metallic systems at low-g have led to unexpected results, and have prompted the analysis of mechanisms which might have disturbed the transformation and led to the unusual results observed. These disturbing effects are generally difficult to analyze even if they occur alone. They are all the more complicated when more than one mechanism is involved. Moreover, other processes that as yet have not been conceptualized may also occur. It is with these factors in mind that we have outlined a program to be carried out on transparent liquid-phase miscibility gap materials for the purpose of acquiring additional insight into

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(a) S. H. Gelles Associates, Columbus, OH 43204

(b) Department of Chemistry, Ohio State University, Columbus, OH 43201

the separation process occurring in these systems. The transparency feature allows the reaction to be viewed directly through light scattering and holographic methods.

BACKGROUND

A number of opaque miscibility gap metallic systems have been made the subject of ground base and flight studies.(1-8) We have been studying aluminum-indium alloys(1,2) in terrestrial and SPAR rocket experiments. In a typical experiment, an alloy of composition within the extremes of the miscibility gap is heated into the single phase liquid field above the miscibility gap (See Figure 1)(2,9) held for a time sufficient to homogenize the alloy and then cooled through the gap at a controlled cooling rate. It was expected that the structure resulting from conducting this heat treatment at low-g would consist of a uniform precipitate contained within a host phase. In the aluminum-rich end of the miscibility gap the dispersed phase would be rich in indium while indium-rich alloys would produce aluminum-rich precipitates in an indium-rich phase. The Al-In alloys processed at 1-g would consist of a layered structure with the indium-rich phase at the bottom and the aluminum-rich phase floating on the top.

Samples of various compositions of aluminum-indium alloys have been processed on both the SPAR II and SPAR V sounding rocket flights. An example of the results obtained is shown in Figure 2 where the macrostructures of an Al-40 and -70 wt. Pct. In alloy processed on SPAR II are compared with their ground base counterparts. The ground base samples possess the expected layered structures but those processed in space did not produce the anticipated uniform dispersions. Instead, as may be seen in Figure 2a, the structure

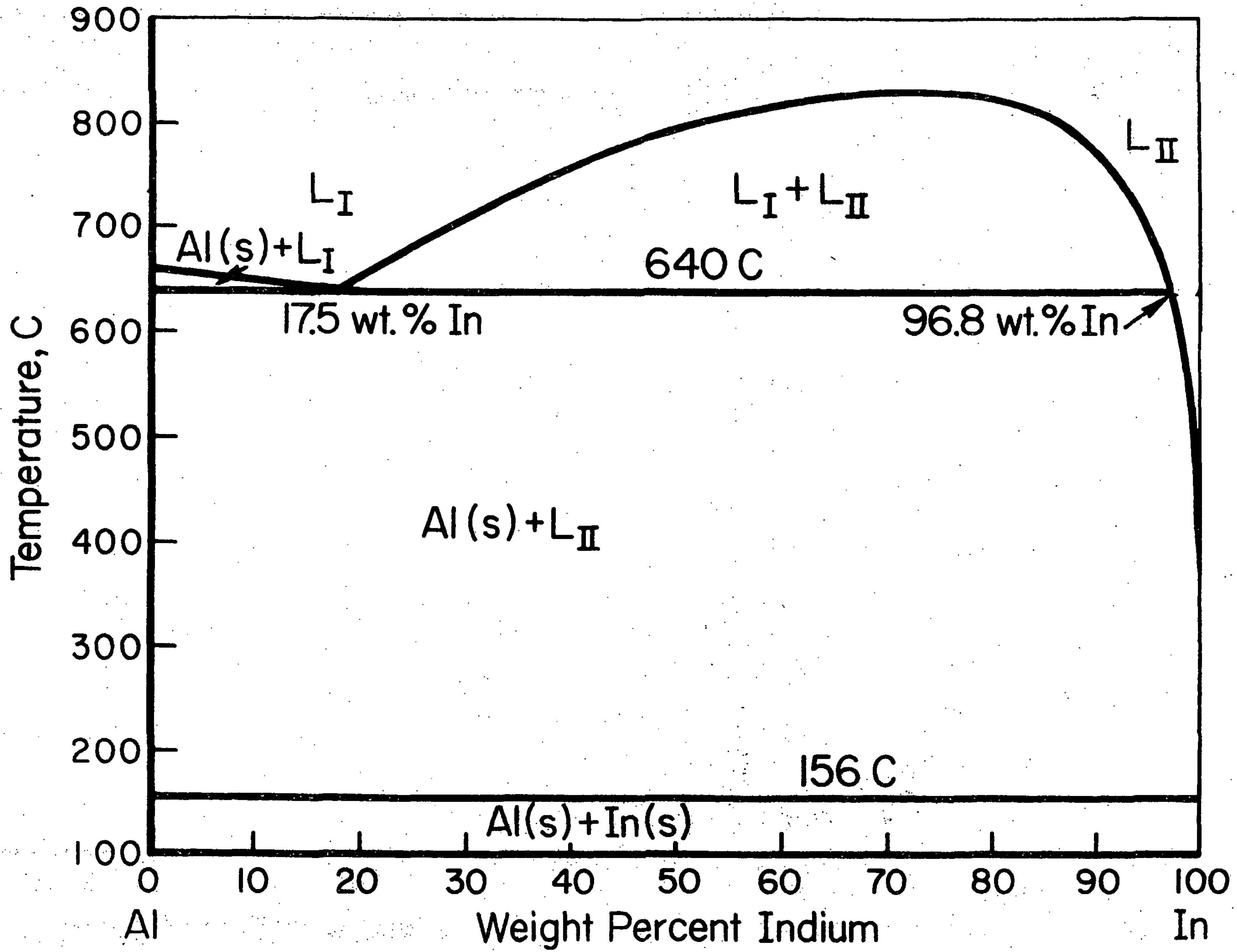
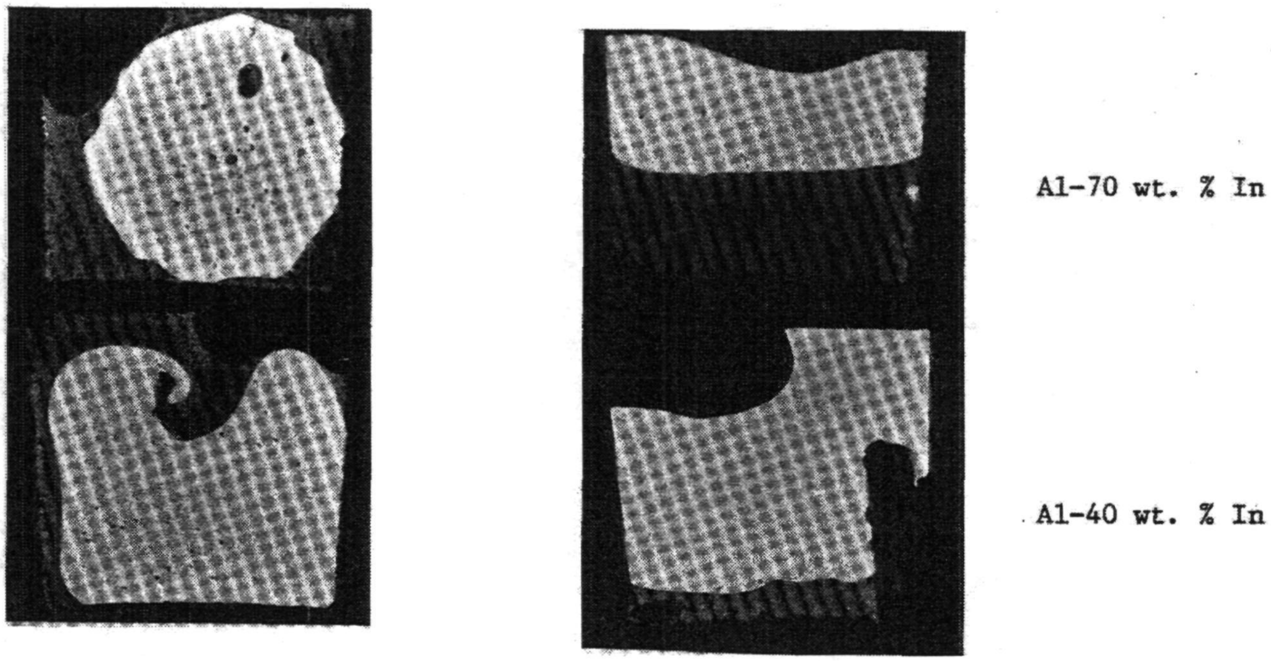


FIGURE 1. THE ALUMINUM-INDIUM EQUILIBRIUM DIAGRAM$^{(2,9)}$



Flight

(a)

Ground Base

(b)

FIGURE 2. MACROSTRUCTURE OF SPAR II Al-In ALLOYS AND THEIR GROUND-BASE COUNTERPARTS

consists of a massively separated aluminum-rich core surrounded by indium-rich material. Observations similar to these have been made in other metallic miscibility gap systems processed at low-g (See for example References 3-5).

Various mechanisms generally involving fluid flow have been proposed to explain the structures of the miscibility gap alloys processed in space. A listing of these mechanisms is presented in Table 1. Some of them have been considered in detail from a theoretical standpoint while others have as yet not been analyzed. For example, detailed calculations have been made on the residual fluid motion present after spin-up and despin in the SPAR rocket experiments with the conclusion that this potential source of fluid motion did not significantly contribute to the development of the observed structures. Similarly, inhomogeneities in the starting Al-In alloys have been ruled out as being contributory after extensive measurements of liquid phase diffusion had been made and after long homogenization times had been applied to the experimental procedure with no discernable difference in results.

Evidence has been obtained that surface tension driven fluid motion has influenced the structure of the Al-In alloys processed in SPAR II and SPAR V. In support of this model, wave-like structures have been observed at the liquid- liquid interfaces and in addition evidence of droplet migration driven by surface tension forces has been presented as shown in Figure 3(2). The alloy illustrated in this figure is an Al-90 wt. pct. In alloy processed aboard SPAR V. The macrostructure consists of two massive aluminum-rich regions surrounded by indium-rich material. Adjacent to the larger aluminum-rich region is an annular area that consists of agglomerating aluminum- rich spheres (See Figure 3b). Further away from the aluminum-rich metal, there

TABLE 1. POSSIBLE MECHANISMS FOR MASSIVE PHASE SEPARATION

Residual Fluid Motion

Surface Tension Drive Flow (Marangoni Effect)

Conventional Convection

Capillarity (Spreading)

Transformation Segregation

Transformation Volume Changes

Nonuniform Starting Composition

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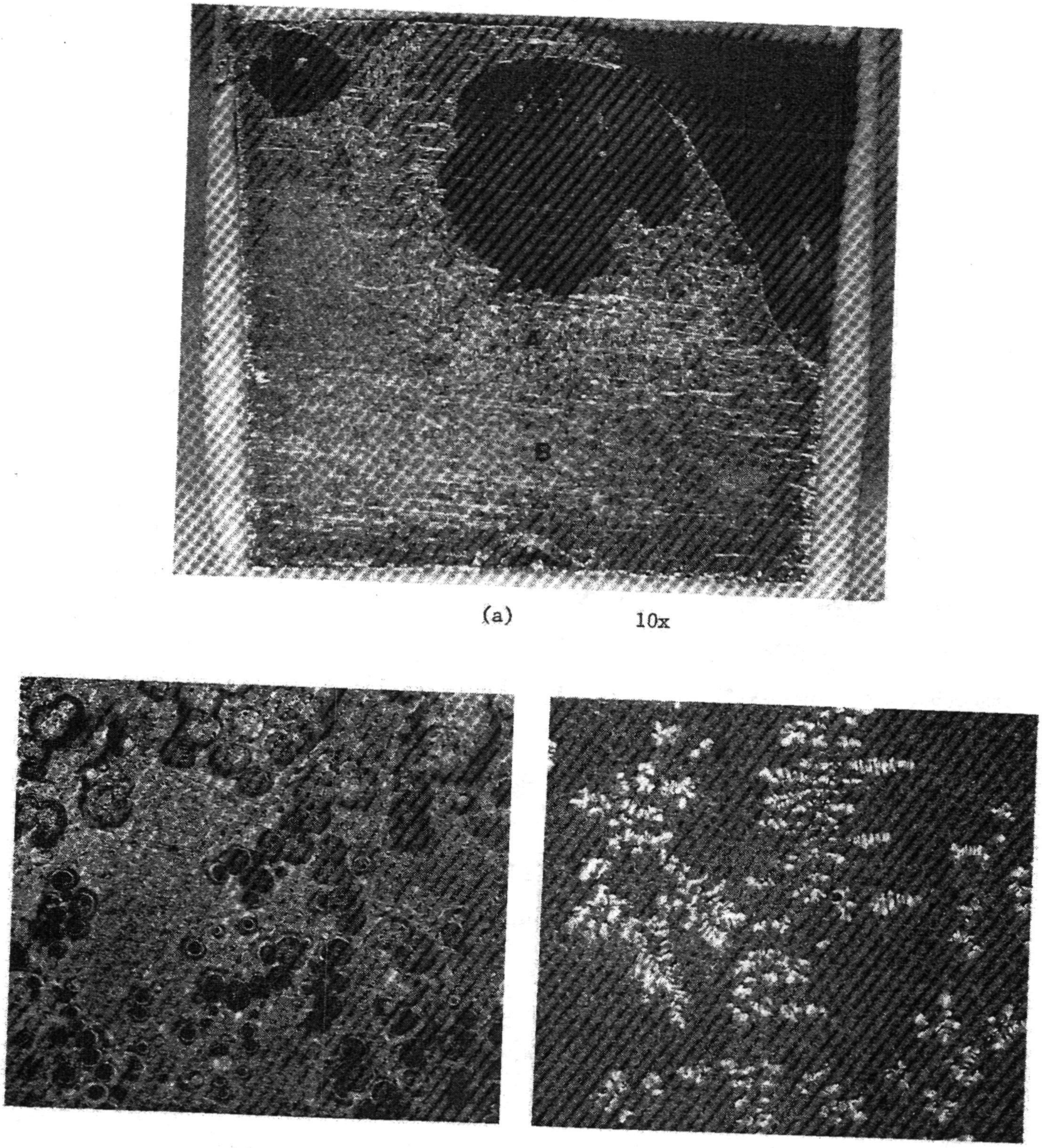

(a) 10x

(b) 100x

(c) 100x

FIGURE 3. STRUCTURE OF Al-90 WT. PCT. In ALLOY PROCESSED ON SPAR V. (a) Macro View of Longitudinal Cross-Section. (b) Microstructure of Region A in (a) and (c) Microstructure of Region B in (a).

in an area that is relatively free of the aluminum-rich spheres (Figure 3 c). These structural observations can be explained by a model consisting of the aluminum-rich spheres migrating to the warmer regions of the molten alloy during cooling through the miscibility gap. Quantitative support for this model has also been obtained.(2)

It is rather difficult to sort out the various phenomena that are contributing to the structural evolution of the liquid-phase miscibility materials. This is especially difficult in opaque systems where generally only the final structure is available for analysis of the mechanisms which might have contributed to its formation. Studies in transparent analogue systems would offer two distinct benefits. First of all, they would allow direct observations of the fluids during transformation and secondly, they would provide systems with a wider range of physical properties so that the importance of various physical parameters can be assessed in terms of phase separation kinetics and emulsion stability. In the following section we outline an experimental program dealing with transparent liquid phase miscibility gap systems which would supplement the present research activities on the metallic systems.

SUGGESTED RESEARCH PROGRAM ON LIQUID PHASE MISCIBILITY GAP SYSTEMS

A study of transparent liquid phase miscibility gap systems would have as its objectives:

1. To view phase-separation in situ in an attempt to determine the mechanism of massive separation previously seen in metallic systems.

2. To determine the effect of material properties on the kinetics of phase separation, on the occurrence of various fluid flow mechanisms and on emulsion stability.

To accomplish these objectives, we are suggesting the following program which can be organized into the following phases.

Phase 1. System Selection

Phase 2. Ground Base Experiments

Phase 3. Flight Experiments

System Selection

This part of the program would be devoted to the very important task of selecting the proper systems for study. In the selection process the most important parameters are the physical properties such as the surface energies and interfacial energies between the two coexisting liquids and their variation with composition and temperature. In addition, fluid flow properties such as viscosities are of importance. Aside from these basic physical properties, it is important to select systems that are convenient to work with, i.e. that have convenient consolute temperatures, miscibility gap widths and heights and which will not create excessive handling problems, due to extreme toxicity, for example, or to a requirement for ultra-purification. Examples of three types of transparent liquid phase misciblity gap systems are shown in Figure 4. Figure 4a shows the more common type with an upper critical temperature, whereas Figure 4b shows one with a lower critical temperature. Figure 4c has both upper and lower critical temperatures.

Ground Base Experiments

It is envisioned that the ground base research would be in three areas.

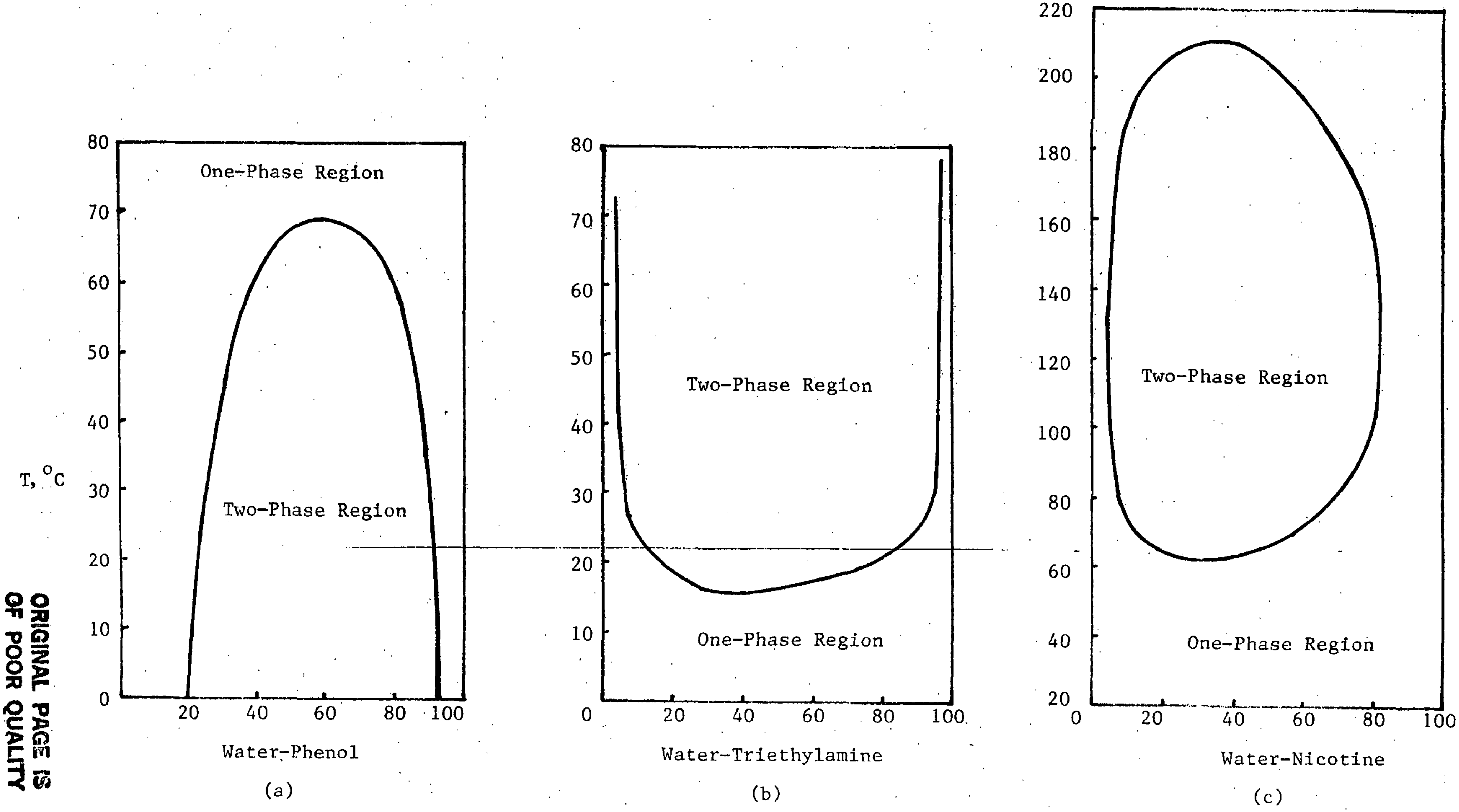

FIGURE 4. EXAMPLES OF TRANSPARENT MISCIBILITY GAP SYSTEMS. (a) Shows an upper critical temperature. (b) A lower critical temperature and (c) both lower and upper critical temperature.

1. System property evaluation.
2. Phase separation kinetics and emulsion stability.
3. Fluid flow mechanisms.

System Property Evaluation

In this portion of the program, the literature dealing with the physical parameters listed in Table 2 would be reviewed for the selected systems and the reliability of pertinent published data would be assessed. In those cases where the data are missing or unreliable, supplementary measurements would be made.

Phase Separation Kinetics

Phase separation kinetics and emulsion stability of various transparent systems having a wide range of material properties would be evaluated by means of light scattering and holographic techniques. The effect of composition within the miscibility gap would be determined in both isothermal and controlled cooling rate experiments. In the isothermal experiments, a chemical mixture making up the transparent system would be cooled or heated from a single phase liquid field into the two phase liquid field where it would be held and monitored as a function of time by such techniques as light scattering. In the cooling rate experiments, the samples would be cooled at controlled rates through the miscibility gap again while monitoring the particle size distribution as a function of time. The results of these experiments would be compared to theoretical models dealing with nucleation, droplet collisions, coalescense and emulsion stability.

Fluid-Flow Mechanisms

Transparency in the systems of interest will provide the opportunity to carry out experiments on the mechanisms of fluid flow which affect the stability and structure of liquid phase miscibility gap systems. Such mechanisms include droplet migration under the driving force of surface tension, thermo-

TABLE 2. PHYSICAL PROPERTIES OF INTEREST IN STUDIES ON TRANSPARENT MISCIBILITY GAP MATERIALS

Phase Equilibra
Viscosities
Interfacial Energies
Thermal Properties
Diffusional Characteristics
Transformation Volume Changes

capillary and solutalcapillary convection, spreading, fluid motion due to volume changes associated with transformations and fluid motion due to coalescense mechanisms. The experimental approach would be supplemented with theoretical modeling.

LOW GRAVITY EXPERIMENTS

Experiments dealing with transparent liquid phase miscibility gap systems at low gravity will be designed with the objective of determining the effect of gravity on the separation kinetics, emulsion stability and fluid flow phenomena associated with the phase separation. The Fluids Experiment System (FES) now being designed would appear to be a suitable apparatus in which to carry out these experiments. Specific experiments dealing with the pertinent mechanisms of fluid flow would probably develop from the ground base studies.

The rationale for conducting these studies at low gravity is to reduce the complications associated with buoyancy effects, conventional convection and their associated contributions to droplet collisions.

ANTICIPATED BENEFITS

The extension of the research on liquid phase miscibility gap systems into studies on transparent systems should provide insight into the mechanisms causing massive separation in metallic miscibility gap alloys. The research should also provide a better understanding of the effect of material parameters on phase separation kinetics, droplet size distribution, and emulsion stability. Since the experiments on transparent systems would allow measurements of the separation process to be made while the reaction is occurring these systems would also be ideal for studying spinodal decomposition.

The research would also provide insight into the fluid flow mechanisms which are active in these systems and which may be accentuated in an acceleration-free environment. With the attaining of an understanding of the material parameters of importance in the phase separation, it will be far easier to select systems of potential technical importance.

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