Dendritic Morphology Observed in the Solid-State Precipitation in Binary Alloys

S. WILAYAT HUSAIN, M. SAEED AHMED, and IHTZAZ QAMAR

The precipitation of γ_2 phase in Cu-Al β-phase alloys has been observed to occur in the dendritic morphology. Such morphology is rarely observed in the solid-state transformations. Earlier it was reported that the γ precipitates were formed in the dendritic shape when Cu-Zn β-phase alloys were cooled from high temperature. The characteristics of these two alloy systems have been examined to find the factors promoting the dendritic morphology in the solid-state transformations. Rapid bulk diffusion and fast interfacial reaction kinetics would promote such morphology. The kinetics of atom attachment to the growing interface is expected to be fast when crystallographic similarities exist between the parent phase and the precipitate. We have predicted the dendritic morphology in the solid-state precipitation in many binary alloy systems simply based on such crystallographic similarities. These alloys include, in addition to Cu-Al and Cu-Zn, the β-phase alloys in Ag-Li, Ag-Zn, Cu-Ga, Au-Zn, and Ni-Zn systems, γ-phase alloys in Cu-Sn and Ag-Cd systems, and δ-phase alloys in Au-Cd system. Of these, the alloys in Ag-Zn, Ni-Zn, Ag-Cd, and Cu-Sn systems were prepared and it was indeed found that the precipitates formed in the dendritic shape.

I. INTRODUCTION

THE formation of dendrites during solidification of metals is a well-known phenomenon. Thermal supercooling in the case of pure metals and the constitutional supercooling in the case of alloys have traditionally been used to explain the instability occurring in the planar interface due to the existing thermal conditions.[1] Mullins and Sekerka were first to introduce the isotropic capillarity, as part of the boundary conditions in the solution of the diffusion equation, to explain the interface stability.[2] Cahn introduced anisotropy in the surface energy and emphasized the role of interface kinetics in the morphological stability of the growing crystals.[3]

The dendritic morphology in the solid-state precipitation has received little attention. Shewmon noted that the dendritic morphologies are rarely observed in the solid-solid systems.[4] Earlier it was reported that the γ precipitates were formed in the dendritic shape when Cu-Zn β-phase alloys were cooled from high temperature.[5] In the precipitation of γ' phase in Ni-base superalloys, it has been noted that, when the alloys are cooled directly to slightly below the solvus temperature and aged isothermally, the precipitates can grow dendritically.[6] Doherty discussed various factors that appear to explain the lack of shape instabilities in all but a few solid-state reactions.[7] In the present work, we first present our observations regarding the precipitation of γ_2 phase in the Cu-Al β-phase alloys. Afterward, we look into the special characteristics of the two alloy systems, Cu-Al and Cu-Zn, in which such morphology has been observed in the solid-state precipitation. Based on these characteristics, we then predict a few other alloy systems in which such morphology should occur. Experimental evidence is also presented to support the hypothesis.

S. WILAYAT HUSAIN, Deputy Director, M. SAEED AHMED, Assistant Engineer, and IHTZAZ QAMAR, Principal Engineer, are with the Dr. A.Q. Khan Research Laboratories, Rawalpindi, Pakistan.
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II. EXPERIMENTAL

In the early part of the present work, the Cu-14 wt pct Al alloys were prepared in a vacuum induction melting furnace. High-purity copper (99.999 pct) was melted in an alumina crucible placed within a graphite suscepter and then pure aluminum (99.999 pct) was added into the melt. After sufficient time for homogenization, the alloy was poured into a copper mold having a very thin zirconia coating. During the latter part of the present work, the alloys were prepared by keeping component metals in a ceramic crucible kept in a sealed stainless steel container which was heated externally. The forms of component metals used and their purity levels are given in Table I. In general, several meltings had to be carried out with adjustment in composition to achieve final composition in the desired range. The castings were homogenized at appropriate temperatures and the compositions of the alloys were confirmed by using an energy-dispersive x-ray spectrometer of an scanning electron microscope. Various samples were cut from the homogenized castings, solution treated, and then directly transferred to another furnace for isothermal precipitation reaction. Table II summarizes the compositions of the alloys and the heat treatments. The appropriate compositions and temperatures, for each binary system, were selected from the respective phase diagrams given in the ASM *Metals Handbook*.[8] Samples for metallography were etched using an appropriate etching solution in each case.

III. RESULTS

We first present the observations regarding the formation of dendritic precipitates in the β-phase alloys in the Cu-Al and Cu-Zn systems.

A. *Cu-Al System*

Figure 1 shows the relevant portion of the Cu-Al phase diagram.[8] In the present work, we are interested in the

Table I. Forms and Purity Levels of Component Metals Used in Preparation of the Alloys

Metal	Purity (Pct)	Metal	Purity (Pct)
Aluminum ingot	99.9	tin shots	99.95
Cadmium rod	99.99	silver foil	99.9
Copper rod	99.95	zinc shots	99.9
Nickel shots	99.97	—	—

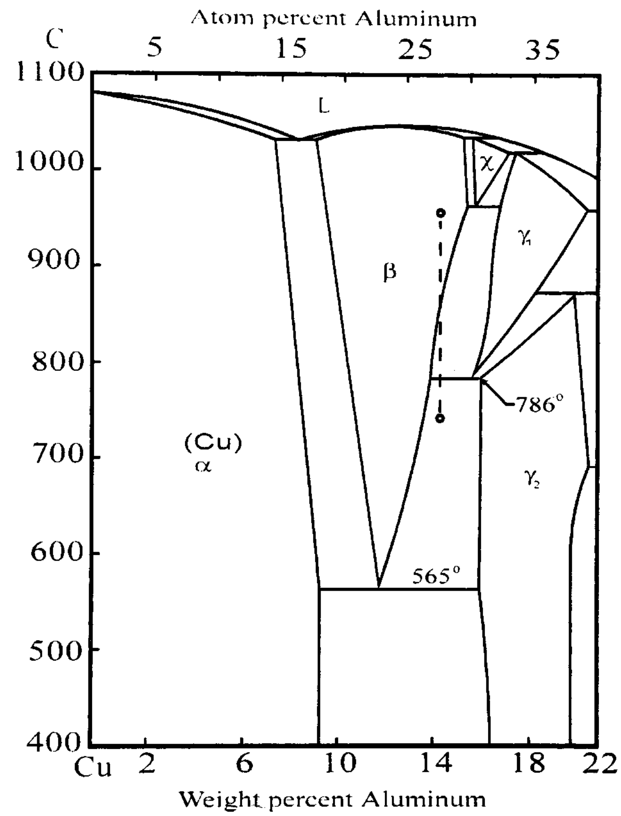

Fig. 1—A relevant portion of the Cu-Al phase diagram.[8]

precipitation of γ_2 phase as depicted by the following reaction:

$$\beta\text{(supersaturated)} \rightarrow \gamma_2 + \beta$$

The dendritic shape of the γ_2 precipitates was earlier reported by the present authors.[9] Figure 2 represents the martensitic structure obtained when the samples are quenched from 950 °C into ice water. This microstructure is presented to show

Fig. 2—Martensitic structure obtained in a Cu-Al sample quenched in ice water from 950 °C. The structure clearly shows the absence of original cast structure.

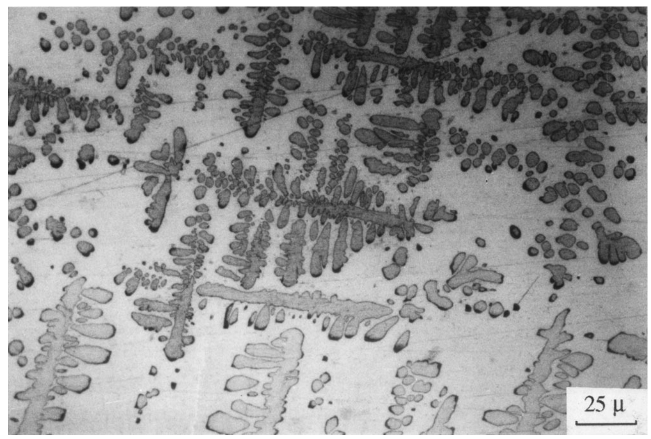

Fig. 3—Dendritic precipitates in a Cu-Al sample cooled in furnace from 950 °C.

that the samples were homogeneous at the solution temperature and that the original cast structure had been eliminated through the homogenization treatment. Figure 3 shows the dendrites of γ_2 phase in a sample cooled in furnace from 950 °C. Next, we present some observations when the β phase is reacted isothermally at 750 °C to precipitate out γ_2 phase in the two-phase field. The composition of the alloy (14 wt pct Al), its solution temperature, and the reaction temperature are shown by the dotted line in the phase diagram in Figure 1. Figure 4 shows the initial stage of precipitation in a sample isothermally reacted for 1 minute and then quenched in ice water. Figure 5 shows the early stage of

Table II. Alloy Compositions and Heat Treatments

	Alloy Composition	Homogenization Treatment	Heat Treatment for Precipitation
1	Cu - 14.0 wt pct Al	6 h at 950 °C	1 h at 950 °C, 1 to 15 min at 750 °C
2	Cu - 52.7 wt pct Zn	8 h at 820 °C	1 h at 820 °C, 15 min at 530 °C
3	Ag - 56.0 wt pct Cd	10 h at 625 °C	2 h at 430 °C, 30 min at 250 °C
4	Ag - 42.5 wt pct Zn	10 h at 650 °C	2 h at 650 °C, 30 min at 450 °C
5	Cu - 31.3 wt pct Sn	10 h at 700 °C	1 h at 700 °C, 15 min at 530 °C
6	Ni - 58.3 wt pct Zn	8 h at 860 °C	1 h at 860 °C, 15 min at 680 °C

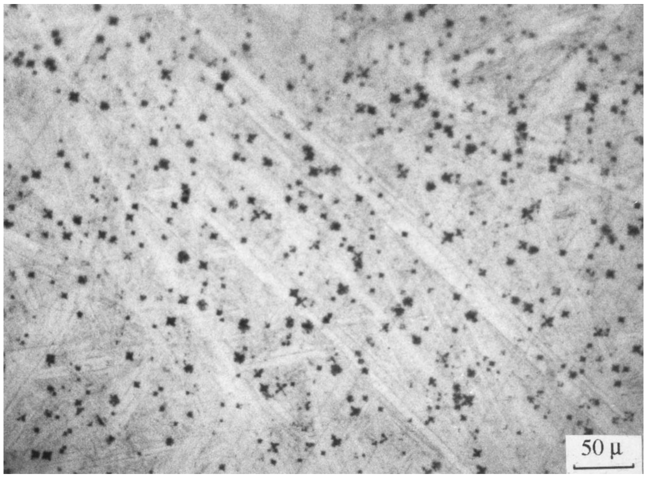

Fig. 4—The initial stage of precipitation in a Cu-Al sample isothermally reacted at 750 °C for 1 min and then quenched in ice water.

Fig. 5—The early stage of dendritic precipitation in a Cu-Al sample isothermally reacted at 750 °C for 5 min and then quenched in ice water.

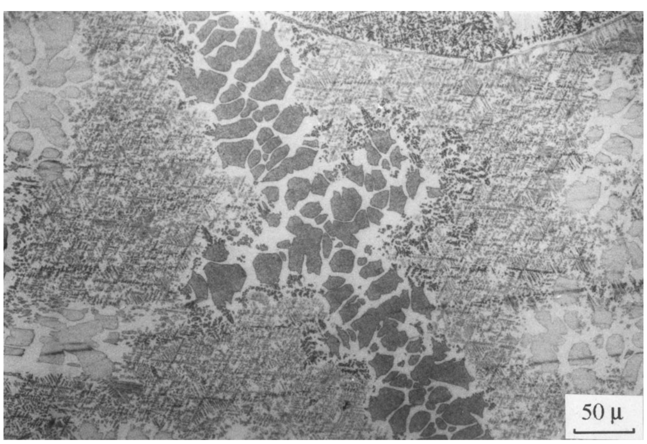

Fig. 6—Dendritic precipitates in a Cu-Al sample isothermally reacted at 750 °C for 15 min and then cooled in air. The large dendrites were formed at 750 °C and the fine dendrites formed during subsequent air cooling.

dendritic precipitation in a sample reacted for 5 minutes and then quenched in ice water. Figure 6 shows the dendritic precipitates in a sample reacted for 15 minutes and then cooled in air. Note that the large dendrites formed isothermally at 750 °C and the fine dendrites formed during the subsequent air cooling. It should be noted that the dendritic arm spacing decreases with increasing cooling rate until a critical rate is reached beyond which β phase directly transforms into martensite without any precipitation, as has been shown in Figure 2.

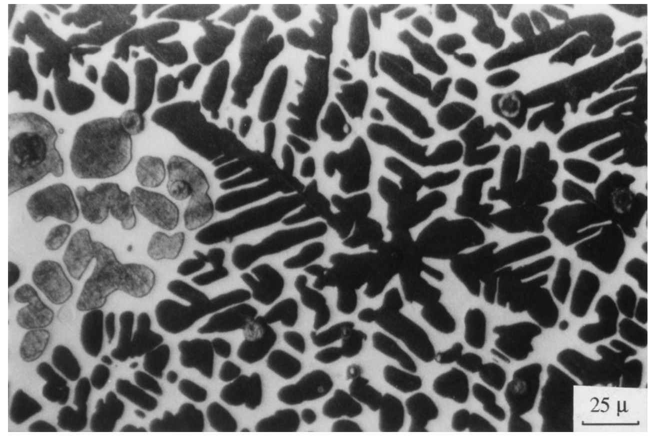

Fig. 7—The dendritic shape of γ precipitates in Cu-52.7 wt pct Zn alloy.

B. *Cu-Zn System*

From the Cu-Zn phase diagram,[8] it is noted that the β-phase alloys with more than 48.9 wt pct Zn would precipitate out γ phase during cooling. Mehl and Marzke[5] observed that γ, isothermally formed in β brass, precipitates as "star-like figures" or dendrites. Malcom and Purdy[10] noted that the γ precipitates were formed in the dendritic shape when Cu-Zn β-phase alloys (containing a small amount of Sn) were cooled from high temperature. The dendritic shape of γ precipitates is clearly seen in Figure 7 obtained from a Cu-52.7 wt pct Zn alloy prepared in the present work. The samples were reacted isothermally at 530 °C after solution treatment at 820 °C.

C. *Other Binary Alloys*

We now present results regarding four other binary alloys, *viz.*, Ag-Cd, Ag-Zn, Cu-Sn, and Ni-Zn, in which we have predicted that the precipitates should have dendritic morphology. The basis of prediction has been discussed in detail in Section IV.

Figure 8 shows the dendritic shape of the δ' precipitates in a Ag-56 wt pct Cd alloy reacted isothermally at 250 °C after solution treatment at 430 °C. The dendritic shape of the γ precipitates is clearly seen in Figure 9 obtained from a Ag-42.5 wt pct Zn alloy. The samples were reacted isothermally at 450 °C after solutionizing at 650 °C. Figure 10 shows the dendritic shape of the δ precipitates in a Cu-31.3 wt pct Sn alloy. The samples were reacted isothermally at 530 °C after solution treatment at 700 °C. The dendritic shape of the γ precipitates is clearly seen in Figure 11 obtained from a Ni-58.3 wt pct Zn alloy. The samples were solutionized at 860 °C and then reacted isothermally at 680 °C.

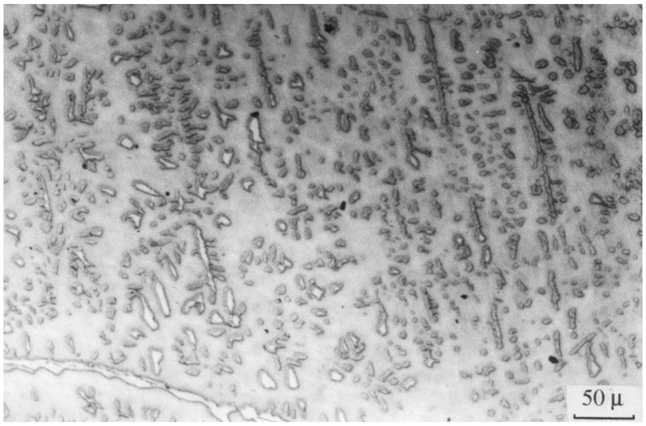

Fig. 8—The dendritic shape of the δ' precipitates in Ag-56 wt pct Cd alloy.

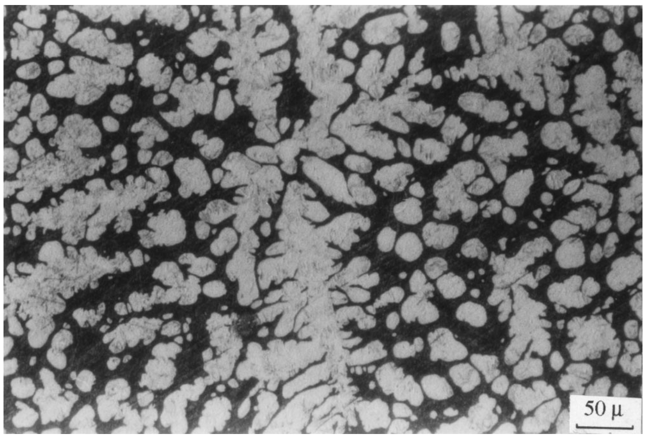

Fig. 9—γ precipitates having dendritic shape in Ag-42.5 wt pct Zn alloy.

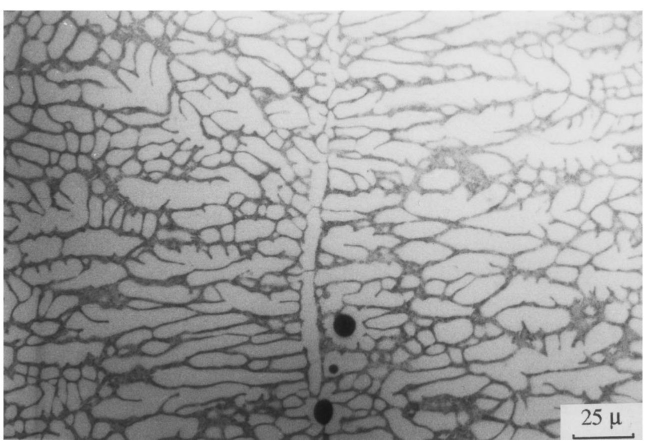

Fig. 10—The dendritic shape of δ precipitates in Cu-31.3 wt pct Sn alloy.

IV. DISCUSSION

The particle shape in the solid-state precipitation may be influenced by various factors such as the rate of diffusion, kinetics of the interfacial reaction, interfacial energy, anisotropy of the parent phase, and the crystallographic features of the precipitate and the parent phase. Some of these factors are implicitly related to each other. For example, similarities in the crystal structures and lattice parameters would result in low interfacial energies. Certain types of crystal lattices would allow faster diffusion as compared to others.

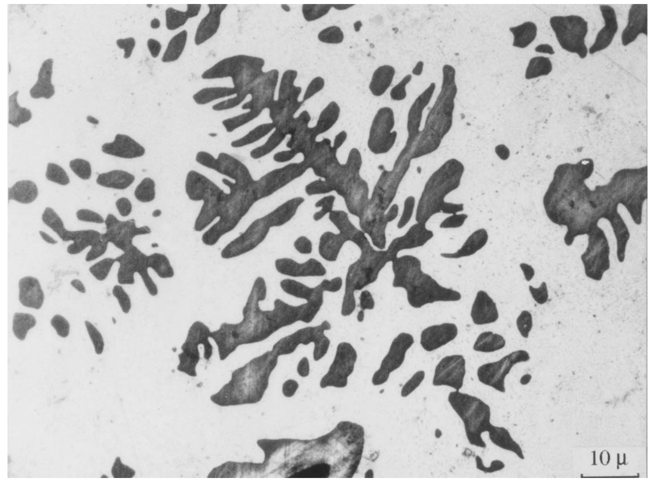

Fig. 11—The dendritic shape of γ precipitates in Ni-58.3 wt pct Zn alloy.

According to Shewmon,[4] if solute diffusion alone determines the growth rate of a precipitate growing from the supersaturated parent phase, the precipitate shape should have characteristics of the dendrites found in solidification. However, this shape is rarely observed in the solid-state precipitation reactions. Therefore, some other stabilizing factor must enter to keep the interface smooth. A slow interfacial reaction will stabilize the interface. In other words, the interfacial stability can be explained by assuming that the movement of atoms across the interface is rate determining (as opposed to the long-range solute diffusion).

The kinetics of addition of atoms to the growing interface plays an important role in determining the morphology of the growing phase.[1] In the case of solidification of molten metals, the kinetics of transfer of atoms from liquid metal to the solidifying crystal is generally very rapid and the result is “nonfaceted” growth morphology. This behavior reflects an independence of the atomic attachment kinetics in relation to the crystal plane involved (a slight tendency to anisotropic growth remains, leading to the appearance of the dendrite trunk and the arms in the low index type crystal directions). On the other hand, substances exhibiting complex crystal structures and the directional bonding form crystals having planar, angular surfaces (facets). This is due to a large difference in structure and bonding between the solid and the liquid phase. In contrast, metals exhibit only very small differences in structure and bonding between the two phases. Therefore, the transition from one phase to the other at the interface is quite smooth.

Therefore, it appears that the kinetics of the attachment of atoms plays a critical role in determining the morphology of a growing phase. The dendritic morphology is favored when this kinetics is fast. As discussed previously, the interface kinetics is expected to be fast when the structures of the phases involved are similar. Therefore, in the case of solid-state precipitation, the crystallographic similarities between the precipitate and the parent phase would favor the dendritic morphology. This includes similarity in the crystal structure, low mismatch in the parameters, and favorable orientation relationships. Note that the structures of the precipitate and the parent phase are, in general, different from each other and, therefore, it is rare to find the dendritic morphology in the solid-state transformations.

Let us consider the crystallographic relationships between the parent phase and the precipitate in the case of Cu-Al and Cu-Zn systems. The high-temperature β phase in both of these systems has a bcc structure. The γ_2 phase in the Cu-Al system has $D8_3$ structure, while the structure of the γ phase in the Cu-Zn system is $D8_2$.[11] Both $D8_2$ and $D8_3$ are the superlattices containing 52 atoms per unit cell. These lattices are basically formed by $3 \times 3 \times 3$ bcc unit cells. The lattice parameters are also closely related; *i.e.*, the lattice parameter of the superlattice (*i.e.*, the precipitate) is almost 3 times the lattice parameter of the parent phase. In other words, the β and γ (or γ_2) lattices are almost identical. Hence, no plane or direction of β could be preferred over others for the formation of γ (or γ_2) precipitates. In other words, there exists a three-dimensional lattice matching in these alloy systems. The three-dimensional matching in the case of β and γ lattices in the Cu-Zn system was first noted by Woo *et al.*, [12] who determined that $(100)_\gamma \| (100)_\beta$ and $[010]_\gamma \| [010]_\beta$. This orientation relationship was confirmed by Malcom and Purdy[10] using electron diffraction.

Therefore, we have an interesting situation in the case of Cu-Zn and Cu-Al β-phase alloys. On cooling to below the solvus temperature, γ (or γ_2) phase gets precipitated out. This precipitation simply requires diffusion of atoms for the slight adjustment of composition. The structure and the lattice dimensions of the precipitate are similar to those of the parent phase. Hence, the diffusing atoms do not face any difficulty in attaching themselves to the growing interface. As a result, the precipitate has dendritic morphology.

Based on the preceding discussion, we formulate the following simple criteria. The dendritic morphology of a precipitate, in the solid-state precipitation, is expected if

(1) a solid solution (say β) gets supersaturated on cooling and forms precipitates of another solid solution (say γ);
(2) β and γ have similar structures, *e.g.*, β is bcc and γ has a cubic superlattice such as $D8_2$; and
(3) the lattice parameter of γ is a simple multiple of the β phase, *i.e.*, $a_\gamma \approx n a_\beta$.

Binary alloy systems complying with these conditions are shown in Table III. These ten alloy systems have been found from the data available in the ASM *Metals Handbook*[8] and the *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*.[11] Note that, in all the cases presented in Table III, the value of n is 3. The lattice types and the values of the parameters, in each case, suggest that there would be three-dimensional matching between the parent phase and the precipitate. The data on orientation relationships in these systems are lacking and, to our knowledge, such matching has been reported for Cu-Zn[12] and Ag-Zn[17] only.

It should be emphasized that fast bulk diffusion is necessary for the dendritic morphology to occur. Diffusion is very rapid in β phases in both Cu-Al and Cu-Zn systems. This is reflected by very large values of diffusion coefficients. For instance, the value of chemical diffusion coefficient for Cu-12.5 wt pct Al at 750 °C is 2.51×10^{-7} cm^2/s, whereas the value of chemical diffusion coefficient for Cu-50 wt pct Zn at 530 °C is 5.24×10^{-8} cm^2/s.[13] Though the diffusion data for secondary solutions are lacking, the alloy systems predicted in Table III are expected to have high diffusion rates. Note that the parent phase in all the cases has a bcc lattice, which generally allows faster diffusion as compared to the close-packed lattices. In addition, all the solute elements have quite mobile atoms. All of these elements (*i.e.*, Al, Zn, Cd, Sn, Li, and Ga) have low melting points, aluminum having the highest (660 °C) and gallium having the lowest (30 °C). The available data does indicate that the coefficients of diffusion for β-Ag-Zn, β-Au-Zn, γ-Cu-Sn, and δ-Au-Cd alloys have quite high values.[14]

In the following, we describe features of the four binary alloys presented in Table III, in which experimental evidence of the dendritic shape of the precipitates has been found in the present work as reported in Section III.

A. *Ag-Cd*

As evident from the Ag-Cd phase diagram,[8] the γ-phase alloys, containing about 55 to 57 wt pct cadmium, would precipitate out δ' phase during cooling below the solvus in

Table III. Crystallographic Features of the Parent Phase and the Precipitate in Binary Alloys in Which Dendritic Morphology is Expected

		Parent Phase			Precipitate			
Number	Alloy System	Phase	Structure Type	Lattice Parameter (nm)	Phase	Structure Type	Lattice Parameter (nm)	Mismatch (Pct)‡
1	Cu-Al	β	A2	0.29564	γ_2	$D8_3$	0.87068	1.8
2	Cu-Zn	β	A2	0.29967	γ	$D8_2$	0.8869	1.3
3	Ag-Cd	γ	B2	0.3332	δ'	$D8_2$	0.9983	0.1
4	Ag-Li	β	B2	0.3169	γ	$D8_{2\text{-}3}$	0.949*	0.2
5	Ag-Zn	β	B2	0.31556	γ	$D8_2$	0.93407	1.3
6	Au-Cd	δ	B2	0.3315	ζ	$D8_{1\text{-}3}$	0.9998	0.5
7	Au-Zn	β'	B2	0.31485	γ	$D8_{2\text{-}3}$	0.9287**	1.7
8	Cu-Ga	β	A2	0.29671	γ	$D8_3$	0.8747	1.7
9	Cu-Sn	γ	DO_3	0.60605†	δ	$D8_{1\text{-}3}$	1.7980	1.1
10	Ni-Zn	β'	B2	0.29143	γ	$D8_{1\text{-}3}$	0.89228	2.0

The data is compiled from Pearson[11] except (*) the parameters for γ phase in Ag-Li, which are taken from Ref. [14]; (**) the parameters for γ phase in Au-Zn taken from Ref. [15]; and (†) the parameters for γ phase in Cu-Sn taken from Ref. [16].

‡The mismatch has been calculated from the available values of lattice parameters. True mismatch would be defined by the values of lattice parameters at the phase separation temperature.

the temperature range of about 470 °C to 230 °C. The dendritic shape of the δ' precipitates is clearly evident in Figure 8.

B. *Ag-Zn*

As seen from the Ag-Zn phase diagram,[8] the β-phase alloys containing Zn in the range of about 38 to 46 wt pct would precipitate out γ phase during cooling. The dendritic shape of the γ precipitates is clearly seen in Figure 9. It should be noted that, as expected, the three-dimensional matching has been confirmed in this system, *i.e.*, the orientation relations are such that $(100)_\gamma \| (100)_\beta$ and $[010]_\gamma \| [010]_\beta$.[17]

C. *Cu-Sn*

The Cu-Sn phase diagram[8] indicates that the hypereutectoid γ-phase alloys (containing Sn in the range of about 27 to 32 wt pct) would precipitate out δ phase during cooling below the solvus (between 590 °C and 520 °C). The lattice matching indicated in Table III suggests that these precipitates would have dendritic shape, and this is clearly seen in Figure 10. It is interesting to note that the parent phase (γ) in this case is already a superlattice with DO_3 structure.[11] This unit cell is composed of $2 \times 2 \times 2$ bcc basic units. The structure of δ phase is cubic with 413 atoms per unit cell and can be considered as a γ-brass type superstructure.[11] It has a very large unit cell composed of $6 \times 6 \times 6$ basic bcc units.

D. *Ni-Zn*

The Ni-Zn phase diagram[8] indicates that the hypereutectoid β-phase alloys (containing about 56.2-61.1 wt pct Zn) would precipitate out γ phase during cooling. The dendritic shape of the γ precipitates is clearly seen in Figure 11.

In short, out of the ten binary systems predicted, we now have the evidence of dendritic morphology of the precipitates in six systems. We are in the process of preparing the alloys corresponding to the remaining four systems, *viz.*, Ag-Li, Cu-Ga, Au-Zn, and Au-Cd. Note that, in all these cases, the value of n is 3. It would be interesting to look for the systems where n is different from 3. One such system is that of nickel-base superalloys in which the value of n is 1. In this system, the ordered fcc phase (*i.e.*, γ' precipitates) and the parent phase (γ) exhibit three-dimensional matching (*i.e.*, cube-cube orientation). The γ' phase shows dendritic morphology when the precipitation is carried out near the solvus temperature.[6]

V. CONCLUSIONS

The phenomenon of the dendritic morphology in the solid-state precipitation has been discussed. The crystallographic similarities between the parent phase and the precipitate have been shown to be a dominant factor giving rise to the dendritic morphology of the precipitates. Based on the crystallographic similarities, ten binary alloy systems were predicted to show such morphology, out of which six have experimentally been verified.

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