

THERMODYNAMIC ASPECTS OF MASSIVE TRANSFORMATIONS IN THE Cu-Ga AND Cu-Zn SYSTEMS

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Abstract—Thermodynamic modeling of the Cu-Ga and Cu-Zn phase diagrams has been used to obtain the temperature and composition dependence of the free energies of phases involved in the massive transformation in these two systems. In both systems, the high temperature b.c.c. β phase is shown to be particularly susceptible to a massive transformation because it becomes more rapidly unstable on cooling, or quenching, when compared with the phases with which it is competing in the phase diagram. It is shown that entropy considerations are the principal cause of this behavior. The driving force for the massive transformations in both systems is shown to be relatively small, being only some 100 J/mol in the Cu-Ga system and 420 J/mol in the Cu-Zn system. These values represent about 0.7% and 1% of the total energy of the β phase, respectively, in each system. The obtained values of the driving energies are discussed in relation to the previous estimates of the driving force for massive transformations in the Cu-Zn system and in relation to the nucleation difficulties and nucleation models in massive transformations.

Résumé—Nous avons utilisé la modélisation thermodynamique des diagrammes de phases de Cu-Ga et de Cu-Zn pour obtenir l'influence de la température et de la composition sur les énergies libres des phases impliquées dans la transformation massive de ces deux systèmes. Dans chacun d'eux, nous montrons que la phase β (cc) de haute température est particulièrement apte à subir une transformation massive parce qu'elle devient plus rapidement instable au cours du refroidissement ou de la trempe que les phases avec lesquelles elle entre en compétition dans le diagramme de phases. Des considérations d'entropie permettent d'expliquer l'essentiel de ce comportement. La force motrice des transformations massives dans les deux systèmes est relativement faible: elle ne vaut qu'une centaine de J/mol. dans le système Cu-Ga, et 420 J/mol. dans le système Cu-Zn. Ces valeurs représentent respectivement environ 0,7% et 1% de l'énergie totale de la phase β dans chaque système. Nous discutons les valeurs que nous obtenons pour les énergies motrices en fonction des estimations antérieures de la force motrice pour les transformations massives dans le système Cu-Zn, des difficultés de la germination dans les transformations massives et des modèles proposés pour cette germination.

Zusammenfassung—Aus den thermodynamischen Modellen der Cu-Ga- und Cu-Zn-Phasendiagramme wurden die Temperatur- und Konzentrationsabhängigkeiten der freien Energie derjenigen Phasen ermittelt, die bei der massiven Umwandlung in diesen Systemen eine Rolle spielen. In beiden Systemen neigt besonders die krz. β -Phase zu einer massiven Umwandlung, da sie bei Abkühlen oder Abschrecken rascher instabil wird also die Phasen, mit denen sie im Phasendiagramm konkurriert. Es wird gezeigt, daß entropische Beiträge die Ursache dieses Verhaltens bilden. Die treibende Kraft der massiven Umwandlung ist in beiden Systemen relativ klein, einige 100 J/Mol im System Cu-Ga und 420 J/Mol im System Cu-Zn. Diese Werte entsprechen nur etwa 0,7% und 1% der Gesamtenergie der jeweiligen β -Phase. Diese Werte werden im Zusammenhang mit früheren Abschätzungen der treibenden Kraft der massiven Umwandlung im Cu-Zn-System und im Hinblick auf die Schwierigkeiten der Keimbildung und die Keimbildungsmodelle der massiven Umwandlungen diskutiert.

1. INTRODUCTION

Following the discovery of massive transformations in the Cu-Ga [1] and Cu-Zn [2, 3] systems, it has been accepted as axiomatic that all such composition-invariant, diffusional phase changes must be driven by a substantial free energy difference between the product and parent phases generated during the quenching of the high temperature parent phase. The phase from which the massive transformations occur

in these systems (and in many similar systems) is the disordered b.c.c. β phase. It has been known for many years following the work of Zener [4] that disordered β phases are particularly temperature-unstable on cooling because of a rapid change in the entropy related term $-TS$ in the free energy equation, related to the large vibrational entropy of the b.c.c. structure. However, the actual values of the free energy difference between the parent β matrix and the

massive phase at the temperature of transformation have not been explored quantitatively, mainly because the pertinent thermodynamic data was lacking.

Recent progress in phase diagram calculations and phase diagram assessment based upon a combination of experimental phase boundary data and thermodynamical modelling often makes it possible to derive reasonably accurate free energy expressions for the phases competing in a given phase diagram. In turn, the knowledge of the free energies at different temperatures has made it attractive to consider in quantitative terms the degree of instability of the undercooled β phase at temperatures corresponding to massive transformations. Of additional interest is the change with composition of the driving force for the transformation and the correlations between this parameter and the observed product structures and their transformation ranges.

The types of massive transformations reported in Cu-Ga [5, 6] and Cu-Zn [2, 3] alloys are summarized in Figs 1(a) and (b), respectively. In the range of compositions near the equilibrium termination of the f.c.c. α phase, the $\beta \rightarrow \alpha_m$ transformation takes place in both systems on quenching. The α_m phase is produced as a metastable, composition-invariant extension of the equilibrium α phase to higher gallium or higher zinc contents. In the Cu-Ga system, in the eutectoid and hypereutectoid range past the equilibrium h.c.p. ζ phase, the $\beta \rightarrow \zeta_m$ massive transformation occurs in addition to the α_m , making the metastable h.c.p. phase field much wider than the equilibrium phase field. There is a wide range of compositions where both the α_m and ζ_m massive products are generated simultaneously and the transformation then occurs as a duplex α_m/ζ_m product referred to as "feathers" [6, 7]. The fact that both these structures are possible indicates that the respective free energies of the α_m and ζ_m phases must be nearly the same [8], but it has not been verified quantitatively.

In the present work we report quantitative data for the massive transformations in the Cu-Ga and Cu-Zn systems following a thermodynamic assessment of the relevant phase boundaries in the phase diagram by the present authors and by Spencer [9], respectively. The magnitude of the driving force is then considered, particularly as it pertains to composition ranges, nucleation difficulties and the known rapid growth of massive transformations.

2. THERMODYNAMIC MODELING OF THE PHASE DIAGRAMS

2.1. Cu-Ga system

The general features of the Cu-Ga phase relationships have been well-established by Hansen [10] and in a subsequent revision by Kittl [11] of the details in the composition region approximately between 20 and 25 at.% Ga. These accurately estab-

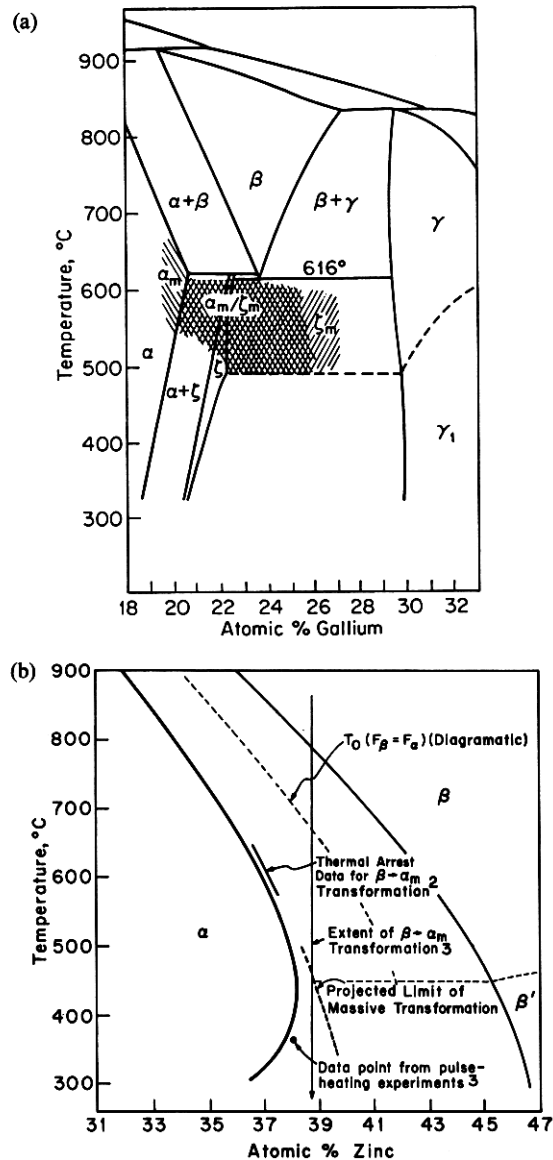


Fig. 1. The regions of the observed massive transformations in copper-based systems: (a) Cu-Ga [5] and (b) Cu-Zn [3].

lished phase boundaries and some additional available thermodynamic data were used to derive expressions for the thermodynamic functions for the various intermediate phases competing for stability in this composition region. The validity of the optimized thermodynamic functions was tested and assessed by comparing the phase boundaries calculated with the use of these functions with the boundaries based upon the experimental data. The well-known "common-tangent" method was used to calculate the boundaries from the thermodynamic functions.

Predel and co-workers [12, 13] have determined enthalpies of mixing of liquid binary Cu-Ga solutions from high-temperature calorimetry. The resulting enthalpy values were fitted to give the following function for the enthalpy of mixing of the liquid

Table 1. Cu-Ga thermodynamic parameters (this study)

Lattice Stability Parameters $G = A + BT$ (J/mol)			
Phase	Element	A	B
L	Cu	0	0
	Ga	0	0
α	Cu	-13054	9.623
	Ga	5021	8.368
β	Cu	-9498	8.786
	Ga	0	8.368
γ	Cu	-9498	8.786
	Ga	0	8.368
ζ	Cu	-12427	10.878
	Ga	-2092	11.381

Excess Gibbs Energies

$$G^{\text{ex}} = X(1-X)[(H_0 - S_0T) + (H_1 - S_1T)X + (H_2 - S_2T)X^2] \text{ J/mol}$$

Phase	H_0	H_1	H_2	S_0	S_1	S_2
L	-72225	101296	-41045	-9.158	44.264	-41.045
α	-73684	63694	0	0	0	0
β	-77033	61058	0	8.281	-25.941	0
γ	15937	-507108	775218	21.859	-91.967	0
ζ	-72559	79484	0	7.812	0	0

Note: Pure liquid Cu and pure liquid Ga have been chosen as standard states. X is the atomic fraction of Ga, and T is the temperature in K.

Cu-Ga alloys

$$H(L) = X(1-X)(-72225 + 101296X - 41045X^2). \quad (1)$$

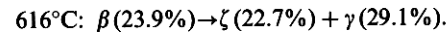
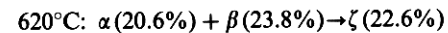
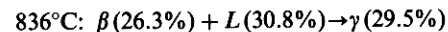
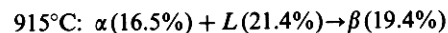
The enthalpy data were then combined with the excess free energies of mixing of the liquid Cu-Ga alloys at 1000 K from Predel [12] to give the following expression for the excess entropy of mixing in the liquid phase

$$S^{\text{ex}}(L) = X(1-X)(-9.158 + 44.264X - 41.045X^2). \quad (2)$$

Excess free energies for the α solid solution were derived by optimizing the free energy function of the liquid phase, as derived above, with the $\alpha/(\alpha + L)$ and $(\alpha + L)/L$ phase boundaries from the Cu-Ga phase diagram. A sub-regular solution approximation for the α -solid solution gave an adequate reproduction of the experimental $\alpha/(\alpha + L)$ and $(\alpha + L)/L$ phase boundaries. The information on the positions of the $\alpha/(\alpha + \beta)/\beta$ phase boundaries between 620 and 915°C and the $\beta/(\beta + L)/L$ phase boundaries between 836 and 915°C was then combined with the free energy functions for the α and L phases, respectively, to derive the function for the excess free energy of the β phase. The excess free energy function for the γ phase was derived in a similar manner from the experimentally established positions on the $\beta/(\beta + \gamma)/\gamma$ and $\gamma/(\gamma + L)/L$ phase boundaries in conjunction with the optimized excess free energy functions for the β and L phases respectively. Finally, the $\alpha/(\alpha + \zeta)/\zeta$, $\zeta/(\zeta + \beta)/\beta$, and the $\zeta/(\zeta + \gamma)/\gamma$ solvi data were combined with the calculated thermodynamic functions for the α , β , and γ phases, respectively, to give the excess free energy

of the ζ phase. The various thermodynamic functions are summarized in Table 1. In all cases, pure liquid Cu and pure liquid Ga were chosen as standard states. Lattice stability parameters of the pure elements in the various phases, also shown in Table 1, were compiled from Kaufman [14, 15] and Ansara [16].

Next, Cu-Ga phase relationships were calculated at selected temperatures in the interval 500–1085°C from the optimized free energy functions for the α , β , γ , ζ and L phases. The calculated phase boundaries, compared with the experimental Cu-Ga phase diagram in Fig. 2, show good agreement with the experimental data, with some exceptions in specific regions. The calculated composition of the β phase at the peritectic temperature of 836°C is shifted from the experimental value toward a higher Cu content by ~0.8 at.%, with a concomitant shift in the $\beta/(\beta + \gamma)$ solvus. However, the general shape of the β -phase stability region has been very well reproduced. Additionally, the calculated stability region for the ζ phase is slightly smaller than that observed experimentally. The various calculated temperature-invariant reactions in the Cu-Ga phase diagram are listed below (all compositions are given in atomic percent):



On the whole, the above values are in excellent agreement with the accepted phase diagram features in this system, as shown in Fig. 2.

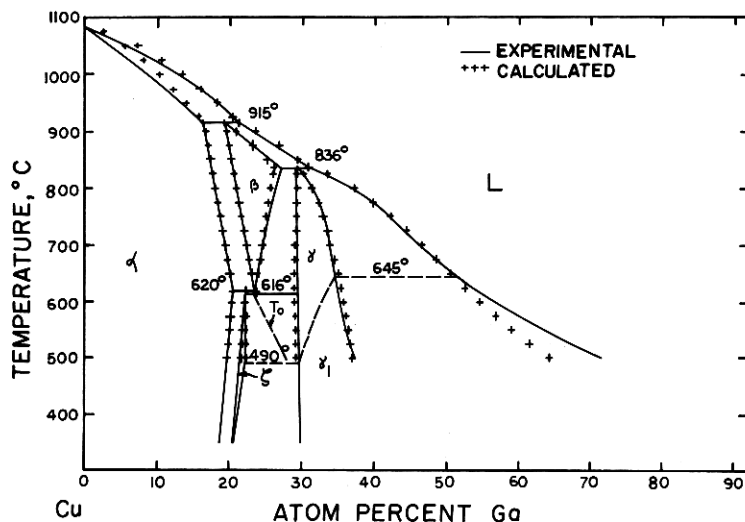


Fig. 2. The calculated phase boundaries compared with experimental boundaries in the Cu-Ga system.

2.2. Cu-Zn system

In a recent publication, Spencer [9] reported a critical assessment and thermodynamic modelling of the Cu-Zn system, based on experimental information on phase relationships and thermodynamic properties. We found this assessment well suited for the present purpose. Excess Gibbs energy functions derived by Spencer for the liquid, α , β , β' and γ phases are listed in Table 2, together with the lattice stability parameters of Cu and Zn in the different phases. Data for only the relevant phases are included in Table 2. The Cu-Zn phase diagram calculated from these functions is reported by Spencer [9] to be in good agreement with the experimental phase diagram given by Hansen [10].

3. ENTROPY CONSIDERATIONS

Table 3 shows the values for the entropies of the α , β , γ and ζ phases in the Cu-Ga system at various

compositions of interest. The excess entropy functions from Fig. 1 were combined with the ideal configuration entropy to derive the entropy values. In all cases, the pure liquid Cu and pure liquid Ga were chosen as standard states, which is the reason why the entropy data appear as negative values in Table 3. As expected, the β phase shows the least negative values of the entropy. On the other hand, if solid Cu and solid Ga are chosen as standard states, the β phase would show the largest positive values. As mentioned above, it has been postulated by Zener [4, 17] that the relatively large vibrational entropy of the β phase is

Table 3. Entropy data for α , β , γ , ζ phases in Cu-Ga (J/mol.K)

At.% Ga	$-S(\alpha)$	$-S(\beta)$	$-S(\gamma)$	$-S(\zeta)$
20	5.212	4.047	3.988	5.568
22	4.966	3.872	4.034	5.267
24	4.740	3.729	4.143	4.992
26	4.532	3.617	4.308	4.741
28	4.342	3.534	4.524	4.514
30	4.168	3.477	4.785	4.310

Table 2. Cu-Zn thermodynamic parameters (from Spencer [86Spe])

Lattice Stability Parameters						
$G = A + BT + CT \ln(T) + DT^2 + E/T$ (J/mol)						
Phase	Element	A	B	C	D	E
L	Cu	-48.7	173.911	-31.28	0	0
	Zn	-3629.1	161.624	-31.38	0	0
α	Cu	-8044.1	135.257	-24.8530	-0.00189325	69454.5
	Zn	-4178.2	98.8181	-20.7359	-0.0062551	-4163.1
β, β', γ	Cu	-4027.1	134.002	-24.8530	-0.00189325	69454.5
	Zn	-3572.2	98.0015	-20.7359	-0.0062551	-4163.1
Excess Gibbs Energies						
$G^{ex} = X(1-X)[H_0 - S_0T] + (H_1 - S_1T)(1-2X) + (H_2 - S_2T)(1-2X)^2$ (J/mol)						
Phase	H_0	H_1	H_2	S_0	S_1	S_2
L	-41104.6	3325.1	19355.1	-13.31409	5.486	15.05038
α	-41661.1	-6160.7	14034.4	-12.83485	2.9274	7.30663
β	-48994.7	4294.6	19531.2	-11.0502	3.48868	20.44399
β'	-54217.6	4474.6	19531.2	-18.13889	3.48868	20.44399
γ	-47463.5	54529.8	91010.5	-11.74479	27.15161	37.87594

Note: X is the atomic fraction of Zn and T is the temperature in K.

Table 4. Relative changes in magnitude of H , $-TS$ and G for the α , β and γ phases in Cu-Zn with change in temperature from 500 to 600°C

At.% Zn	Phase	ΔH 500-600°C	$\Delta(-TS)$ 500-600°C	ΔG 500-600°C
40	α	-226	824	598
	β	-225	658	433
44	α	-213	820	607
	β	-212	664	452
50	β	-192	665	473
	γ	-192	681	489
54	β	-178	659	481
	γ	-179	721	542

Note: The units are in J/mol.

responsible for its increasing stability with increasing temperature, because of the larger contribution to the $-\Delta(TS)$ term in the free energy function. The present set of thermodynamic parameters are entirely consistent with this interpretation. Since the enthalpy of mixing of the various competing phases can be considered to be relatively temperature-independent, the magnitudes of the entropy of mixing and the vibrational entropy determine the relative stability of the phases. From the entropy values in Table 3, it is evident that, with increasing temperature, the competition between α , β and γ phases is such that the free energy curve for the β phase moves up at a relatively slower rate than those for α and γ . In other words, increasing temperature causes the free energy curve for the β to lag with respect to the curves for the α and γ . This results in an increasing homogeneity range for the β phase with increasing temperature, thereby producing the characteristic V-shaped phase field. This is clearly seen in the Cu-Ga phase diagram of Fig. 1 and it also occurs in all known β -brass type alloys based on the noble metals [18]. Of course, the converse will be true if temperature is decreased. The β phase may be expected to become more rapidly unstable on cooling or quenching than the phases with which it is competing in the phase diagram. Thus, the onset of a massive transformation is particularly favorable when the β -phase type alloys are subjected to rapid quenching. Furthermore, even though there are other situations in phase diagrams where the positions of the respective phase fields make it possible to expect a composition-invariant phase change in principle, it is not surprising that the majority of known rapid massive transformations occur when the quenching of the high temperature b.c.c. phase is involved.

In the case of the Cu-Zn phases, both the enthalpy and entropy values show a temperature dependence. As such, it is not immediately evident from the data that the entropy of mixing determines the relative stability of the various phases. In this instance, it is useful to compare the relative changes in magnitude of the entropy as well as the enthalpy of the competing phases in response to an increase in temperature. Table 4 compares the ΔH , $\Delta(-TS)$ and ΔG values for the α and β phases and the same quantities

for the β and γ phases at two representative compositions for an increase in temperature from 500 to 600°C. From this data, it is clear that the $(-TS)$ term in predominantly responsible for the shift in the Gibbs energy curves with increasing temperatures. Additionally, it is seen that, at a given composition, the change in $(-TS)$ values for the α and γ phases is larger than that for the β phase, indicating an increasing homogeneity range for the β phase with increasing temperature. This is consistent with the interpretation offered for the Cu-Ga system.

4. DRIVING FORCES AND COMPOSITION RANGES OF MASSIVE TRANSFORMATION

4.1. The Cu-Ga system

The temperature for the onset of massive transformations in the Cu-Ga system has not been established with great precision and it is likely to vary somewhat with the cooling rate [1, 5, 8, 19, 20]. However, the available data indicates a fairly monotonic and slightly decreasing trend with composition, approximately 20–80°C below the equilibrium eutectoid temperature of 618°C. Since in the present modeling calculation the eutectoid temperature has been derived as 616°C, it seems appropriate to consider the free energy relations at a temperature about 40°C below the eutectoid value. In Fig. 3 the respective trends with composition for the free energies of the competing phases are shown at 576°C and the corre-

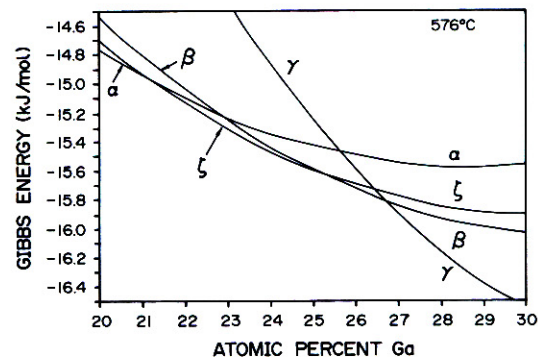


Fig. 3. The respective trends with composition for the free energies of the competing phases in the Cu-Ga system at 576°C.

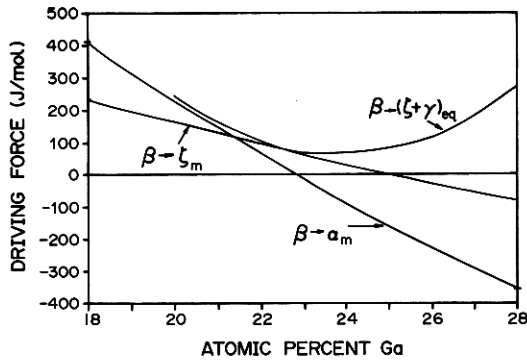


Fig. 4. The driving free energy for the massive transformations in Cu-Ga alloys.

sponding behavior of the driving free energy terms is plotted in Fig. 4. These trends remarkably support the experimental data. The $\beta \rightarrow \alpha_m$ transformation is favored energetically below about 21 at.% Ga, to be followed by a mixed α_m/ζ_m range where the driving force is about the same for both types, and by the $\beta \rightarrow \zeta_m$ transformation when the free energy for the α_m phase transformation is no longer favorable. The calculated respective T_0 trend for the β/ζ transformation is plotted in Fig. 2, and it again behaves as expected. A comparison of the approximate experimentally established transformation temperature data and the $T_0^{\zeta/\beta}$ trend indicates that the massive transformation is in full progress some 20–30°C below T_0 . The driving force for the $\beta \rightarrow \zeta_m$ transformation vanishes when the respective G^β and G^ζ curves cross between 24 and 25 at.%.

The remarkable outcome of the present calculation is the quantitative information on the driving free energy for the transformation. The $\Delta G^{\beta \rightarrow \zeta}$ quantity (Fig. 4) in the composition range where the respective $\beta \rightarrow \zeta_m$ massive transformation occurs with well known ease is only some 100 J/mol, which is a very small fraction (0.7%) of the total free energy ($\sim 15,000$ J/mol) of the phases involved (Fig. 3). Yet, this driving force must be utilized for both the nucleation and growth processes of the transformation. Since a martensitic transformation occurs from the β phase when the quenching rate is sufficient to suppress the massive transformation [1, 11, 19] it is not possible for the $\Delta G^{\beta \rightarrow \zeta}$ term to be increased substantially above 100 J/mol in this system by additional undercooling.

4.2. The Cu-Zn system

The approximate position of the $\beta \rightarrow \alpha_m$ massive transformation, obtained from Massalski *et al.* [3], is shown in Fig. 1(b). The thermal arrest data indicates that in this system the $\beta \rightarrow \alpha_m$ transformation occurs some 100–120°C below $T_0^{\alpha/\beta}$, which provides a substantially larger undercooling compared with Cu-Ga alloys. In the vicinity of 38 at.% Zn, the extrapolated onset-temperature for the massive transformation is about 450°C, which is about 150°C below the re-

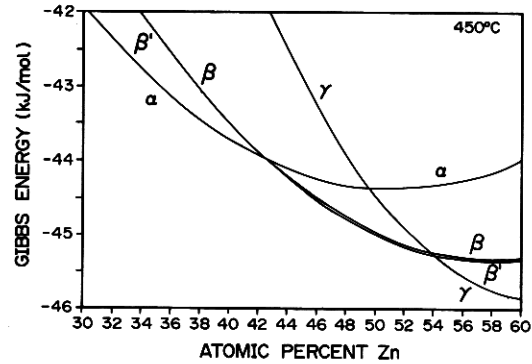


Fig. 5. The respective trends with composition for the free energies of the competing phases in the Cu-Zn system at 450°C.

spective $T_0^{\alpha/\beta}$. Figure 5 shows the Gibbs energy vs composition curves for the competing phases at 450°C in the composition range 30–60 at.% Zn. The calculated T_0 values for the (α/β) equilibrium agree well with the trend shown in Fig. 1(b). The driving force values for the $\beta \rightarrow \alpha_m$, $\beta \rightarrow (\alpha + \beta)_{eq}$ and $\beta \rightarrow \gamma$ transformations are plotted in Fig. 6. The trends indicate that the driving force for the $\beta \rightarrow \alpha_m$ transformation vanishes at ~ 43 at.% Zn. Its value is ~ 420 J/mol at 38 at.% Zn, which is about 1% of the total Gibbs energy of the β phase $-43,000$ J/mol, and is some four times larger than the corresponding $\Delta G^{\beta \rightarrow \zeta}$ in Cu-Ga alloys.

5. NUCLEATION AND GROWTH ENERGETICS

The rate controlling process for massive transformations has been stated to be the nucleation event [21]. Plichta *et al.* [22] in their recent review of the massive transformation have summarized the experimental work on nucleation kinetics. They concluded that within the framework of the various extensions of the classical solid state nucleation theory, incoherent nucleation of the massive phase appears to be impossible. This is because the surface energy of the incoherent nucleus is too large relative to the driving force for nucleation. Indeed, several assumptions (e.g. pillbox model; reduction in the number of

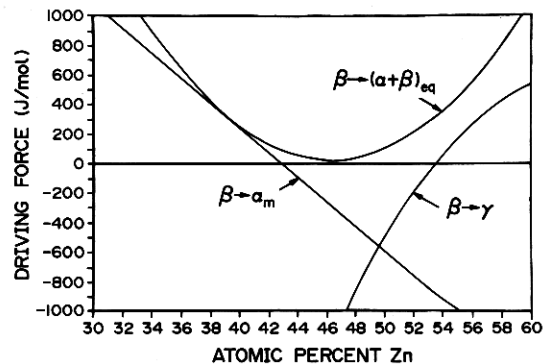


Fig. 6. The driving free energy for the massive transformations in Cu-Zn alloys.

heterogeneous grain boundary nucleation sites; no strain energy contribution, etc.) are necessary to bring the calculation of nucleation rate into line with some of the experimentally observed nucleation rates, at least in the Ti-X alloys [23].

In our work, we calculate ΔG_v for $\beta \rightarrow \alpha_m$ at 723 K in Cu-Zn to be about -420 J/mol (see Fig. 6). The value that Plichta *et al.* [22] used was about -431 J/mol for the same system. Thus, their estimate of nucleation rate would not be very different from ours, using the same nucleation rate equations. The fact that our value of ΔG_v for Cu-Zn correlates well with that used by Plichta *et al.* (derived from Karlyn *et al.* [24]) shows that the thermodynamic analysis used here has yielded a consistent free energy description.

It is assumed that nucleation in massive transformations can only arise as a result of reductions of the surface energy part in the activation energy term ΔG^* , brought about by at least partial coherence of the massive phase nucleus with the transforming matrix, the obvious sites for such nucleation are the grain boundaries. It has been proposed [22] that coherence at the grain boundary with respect to at least one of the matrix grains makes it possible to construct potential nuclei shapes that would have sufficiently low ΔG^* for heterogeneous massive transformation. However, the recent work by Caretti *et al.* [25] clearly indicates that while nuclei formed at grain boundaries (and edges and isomers) are likely to hold a special orientation relationship with one of the matrix crystals, nucleation in Cu-Ga alloys also occurs within the bulk volume of the matrix grains. The question to be considered therefore is whether or not such volume nucleation can be regarded as homogeneous, or whether such observed volume nucleation is catalyzed by some type of defects (for example dislocations) which lower the activation energy? Nucleation features of massive grains formed in the bulk volume of the parent grains in Cu-Ga alloys do not indicate any definite crystallographic orientation relationship [1, 25]. Therefore, the particular features of bulk massive phase nucleation and growth deserve further careful study.

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