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Metastable extension of solid solubility of alloying elements in silver

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Abstract

The metastable extension of the solid solubility in silver of alloying elements including simple metals, transition metals and rare earth metals has been evaluated by means of measurements of the lattice parameters of rapidly solidified alloys made of individual metals with silver at a cooling rate of 10^6 K s^{-1}. Several regular features of the solubility extension were studied. In silver-rich peritectic alloys containing simple metals, the metastable extended solid solubilities reach or come close to the solute concentration corresponding to an electron concentration $e/a = 1.4$. For rare earth elements, the extension is restricted by the atomic size factor. The extended solid solubilities decrease linearly with increasing difference between the atomic radii of the solute and solvent, that is, they increase linearly as the lanthanide contraction increases. For silver-rich monotectic alloys containing transition metals, the extended solid solubilities are inversely proportional to the respective surface tension ratios, or to the solute-to-solvent electron density ratios in the Seitz atomic cell. The relationship between the metastable extension of the solid solubility and the phase diagram is discussed and some simple empirical rules are proposed for the eutectic, peritectic and monotectic systems.

1. Introduction

In 1952, Falkenhagen and Hofmann [1] studied the solid solubilities of alloys under conditions of rapid solidification. They found that the solid solubilities in aluminium of the transition metals of the first long period increased significantly when the alloy melt was drawn into a copper mould kept at liquid nitrogen temperatures. In 1960, Duwez *et al.* [2] observed a metastable extension of the solid solubility in simple eutectic Ag–Ge and Ag–Si alloy systems, and a continuous series of solid solution alloys were formed in the simple eutectic systems Ag–Cu and GaSb–Ge when these alloys were solidified at a cooling rate of about 10^{6-8} K s^{-1}. Since then, this metastable extension of the solid solubility following rapid solidification has been the subject of much research. It is the basis of a new method for developing new materials with high strength. However, the general rules for the occurrence of this solubility extension have rarely been studied, even though increasing amounts of data were being reported in the literature [3, 4].

Research into the general rules governing the extension of solubility brought about by rapid solidification is important for both practice and

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theory. It provides not only a basis for the choice of constituents for developing new alloys, but also a deeper understanding of the interaction between the constituents in an alloy. This paper is a report of the results from a systematic study of the metastable extension of the solid solubility of various solutes in silver. The solute elements are divided into three groups: (1) simple metals, including aluminium, bismuth, cadmium, gallium, germanium, indium, lead, antimony, tin and zinc; (2) rare earth elements, including yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium and erbium and (3) transition metals, including iron, cobalt, nickel, chromium, manganese and zirconium. A number of general rules and factors which influence the extension of the solid solubility will be discussed.

2. Experimental procedure

High purity elements (99.999% for silver, 99.99% for simple and transition metals and 99.9% for rare earth elements) were used to prepare master alloys. The alloys containing simple and transition metals were each melted in an Al_2O_3 crucible under an argon atmosphere by means of a high frequency current. The alloys containing rare earth (RE) elements were melted in an arc furnace under an argon atmosphere to avoid contamination from the crucible. Chemical analysis indicated that the difference between the nominal and the actual concentration was in the range 0.3–0.5%. Spun ribbons of alloys containing simple and transition metals 0.03–0.05 mm in thickness and 2–4 mm in width were made by the melt-spinning technique. Splat foils of alloys containing rare earth elements 0.05–0.07 mm in thickness were made by the arc-melt hammer and anvil technique. The secondary dendritic spacings in the splat foils of Ag–RE alloys were about 0.25–0.3 μm. By analogy with the dependence of the secondary dendritic spacing in copper alloys on the cooling rate [5], it was estimated that the cooling rate of the splat foils of Ag–RE alloys was of the order of 10^6 K s^{-1}.

A Riguku D–S and Geigerflex D/Max–rA Ru 200 diffractometer and 2155 R5 angulometer were used for X-ray diffraction experiments. The lattice parameters were calculated on a Z–80 microcomputer. The method of least squares was used to eliminate the errors. The lattice parameter of pure silver in a rapidly quenched state is 0.40860 ± 0.00002 nm.

3. Results

The lattice parameter method was used to determine the metastable extended solid solubility. The lattice parameter changes continuously and smoothly in the single solid solution phase region with increasing solute content but remains constant in the duplex phase region.

3.1. *Metastable extended solid solubility of simple metals in silver*

The dependence of the lattice parameters of rapidly solidified silver alloys containing simple metals on the concentration of solutes is shown in

Fig. 1. Figure 1 also shows the data reported in refs. 6–8 (open circles) for comparison with the data obtained in the present study (full circles). Table 1 shows the equilibrium and metastable extended solid solubilities in the alloys studied. It shows that the extension of the solid solubility of the simple metals in silver differs in amount, with gallium being an exceptional case.

3.2. Metastable extended solid solubility of rare earth elements in silver

The atomic radii of rare earth elements are in the range 0.175–0.198 nm and thus are much larger than that of silver (0.144 nm), so that the lattice parameter of the solid solution increases with increasing rare earth element concentration in the single-phase region and remains constant in the duplex-phase region. The concentration corresponding to the inflection point in a plot of lattice parameters *vs.* rare earth element concentration was chosen as the metastable extended solid solubility and these values are listed in Table 2. It can be seen that the solid solubilities of rare earth elements in silver increase in various degrees under rapid solidification. These extensions are smaller for light rare earth elements than for heavier ones. This trend is similar to the trend in their equilibrium solid solubilities.

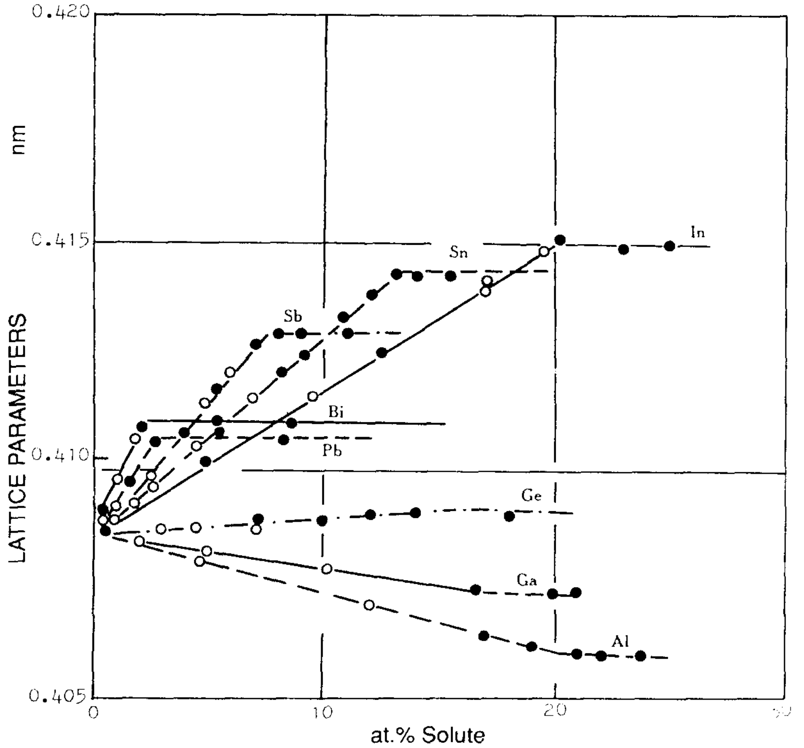

Fig. 1. Lattice spacing *vs.* solute concentration for alloys based on silver, containing simple metals; filled circles, this study; open circles, refs. 6–8.

TABLE 1

Comparison between equilibrium and metastable extended solid solubility of simple metals in silver

Solute	Phase diagram	Eutectic or peritectic point (at.%)	Equilibrium solid solubility		Metastable extended solid solubility	
			at.%	*e/a*	at.%	*e/a*
Al	Peritectic	20.5	17.84	1.36	20.5	1.41
Bi	Eutectic	95.3	0.83	1.023	2.25	1.09
Cd	Peritectic	41	37.4	1.37	40	1.42
Ga	Peritectic	22	18.7	1.37	16.5	1.34
Ge	Eutectic	25.9	9.6	1.29	13.5	1.405
In	Peritectic	24	20	1.40	20	1.40
Pb	Eutectic	95.3	0.8	1.024	2.9	1.09
Sb	Peritectic	8.8	7.2	1.29	7.5	1.30
Sn	Peritectic	13	11.5	1.34	13	1.39
Zn	Peritectic	36.7	32.1	1.32	37.5	1.38

TABLE 2

The metastable extended solubility and data from phase diagrams for Ag–Re alloys

RE solutes	Equilibrium solubility[a] C_{eq} (at.%)	Extended solubility C_s (at.%)	Eutectic concentrations C_{eu} (at.%)
Y	1.31	2	11.5
La	0.05	1	10.0
Ce	0.05	1.5	10.0
Pr	0.05	2.5	9.2
Nd	0.23	3.0	10.5
Sm	0.42	3.5	11
Gd	0.95 [10]; 2 [11]	5.0	11
Tb	1.12	5.0	11
Dy	1.3	5.4	12
Er	3.6	6.0	11.5

[a] These data are taken from ref. 9.

3.3. Metastable extended solid solubility of some transition metals in silver

The atomic radii of iron, cobalt, nickel, chromium and manganese are smaller than that of silver, so that the lattice parameters of the solid solutions decrease with increasing solute concentration. The metastable extended solid solubilities of these elements in silver are listed in Table 3.

The heats of mixing of liquid Ag–M (M ≡ Fe, Co, Ni, Cr, Mn) alloys are positive, so that there are miscibility gaps in their liquid alloy ranges. The solubilities of nickel, chromium and manganese in silver at their monotectic temperatures C_l are also listed in Table 3. (We did not find the C_l values

TABLE 3

Comparison of equilibrium and metastable extended solid solubility (C_{eq} and C_s) of certain transition metals in silver

Solute	Eutectic concentration C_{eu} or solubility at monotectic temperature C_l (at.%)	C_{eq} (at.%)	C_s (at.%)	Heat of mixing in liquid alloys at equiatomic concentration[a] ΔH_M (kcal mol^{-1})
Zr	2.9 (C_{eu})	0	6.0	−6.8 (eutectic)
Fe	– (C_l)	0	1.0	6.2 (monotectic)
Co	– (C_l)	0	1.5	4.2 (monotectic)
Ni	3 (C_l)	0	1.5	3.5 (monotectic)
Cr	15 (C_l)	0	3.0	5.7 (monotectic)
Mn	50.3 (C_l)	47	48	2.4 (monotectic)

[a] Calculated from the formula given in ref. 12.

for iron and cobalt in the literature). It can be seen that the extended solid solubilities of the above elements in silver are limited by their C_l values. The silver-rich Ag–Zr alloy is a eutectic system with a large negative heat of mixing ΔH_M; the solid solubility of zirconium in silver has quite a large extension.

4. Some factors influencing the metastable extension of solid solubility in silver

In the equilibrium state, the factors influencing the solid solubility are the electron concentration, electronegativity and atomic size etc. These factors also have an influence on the metastable extended solid solubility.

4.1. Electron concentration rule

Duwez [13] and Anantharaman and Suryanarayana [3] pointed out that the maximum solid solubilities of simple metals in the precious metals copper, silver and gold are related to the valence electron concentrations e/a of the alloys. The solid solubility limit corresponds to $e/a = 1.4$.

The silver-rich terminal solid solutions containing the simple metals zinc, cadmium, aluminium, indium and tin are peritectic-type systems, in which the first electron compounds formed at $e/a = 1.5$ are as shown in Table 4. The metastable extended solid solubilities of these alloys obey the electron concentration rule, namely, their C_s values reach or come close to the value $e/a = 1.4$. Once the equilibrium solid solubility of a certain alloy has reached $e/a = 1.4$, such as in the Ag–In system, its solid solubility shows no extension under rapid solidification. This means that the first electron compounds with $e/a = 1.5$ in peritectic systems represent the limit to any further extension of the solid solubility. In fact, the electron compound with $e/a = 1.5$ corresponds to a sort of "solid solution" based on a particular stoichiometric composition

TABLE 4

C_s and other parameters of peritectic alloys of silver with some simple metals

Solute	C_{eq}		C_s		Electron compound		
	at.%	*e/a*	at.%	*e/a*	A_mB_n	*e/a*	Structure
Zn	32.1	1.32	37.5	1.38	AgZn	1.5	h.c.p.
Cd	37.4	1.37	40	1.42	AgCd	1.5	h.c.p.
Al	17.84	1.36	20.5	1.41	Ag_3Al	1.5	h.c.p.
In	20	1.40	20	1.40	Ag_3In	1.5	h.c.p.
Sn	11.5	1.34	13.0	1.39	Ag_5Sn	1.5	h.c.p.
Sb	7.2	1.29	7.5	1.30	Ag_7Sb	1.5	h.c.p.
Ge[a]	9.6	1.29	13.5	1.405	Ag_5Ge	1.5	h.c.p.

[a] A metastable h.c.p. intermediate phase Ag_5Ge occurs in simple eutectic Ag–Ge systems under rapid solidification [3].

ratio. The range of composition is also extended by different amounts under rapid solidification. In general, the metastable extension of the terminal solid solution is larger than that of the compound. As a result the metastable extended solid solubility is closer to the theoretical value of $e/a = 1.4$ than the equilibrium solid solubility. The Ag–Ga alloy system is an exception in which $C_s < C_{eq}$ (a similar situation occurs in the Al–Zn system etc. [3]). In addition, the extension of the solid solubility is less for Ag–Sb alloys. These observations may be related to a tendency towards a greater extension of the intermediate phase. The metastable extended solid solubility of the Ag–Ge eutectic alloy also reaches $e/a = 1.4$; this is because of the formation of an h.c.p. metastable intermediate phase under rapid solidification [3]. Its solute concentration is in the range 10–30 at.%Ge corresponding to $e/a = 1.3$–1.9. In other words, the metastable h.c.p. phase is an electron compound with $e/a = 1.5$ whose stoichiometric composition can be written as Ag_5Ge. The solid solubility extension is smaller in eutectic systems composed of silver with bismuth or lead. This could be a result of the larger difference in atomic sizes. With a coordination number of 12 an atom of metallic bismuth is 17% larger, and an atom of metallic lead 21% larger, than one of silver.

4.2. *Influence of atomic size*

An important prerequisite for the formation of an extensive solid solution range in an equilibrium state is that the difference between the atomic radii of the solvent and solute should be less than 14%. Obviously, the atomic size difference is also an important factor restricting the metastable extension of the solid solubility. Examples include the Ag–Bi and Ag–Pb alloys discussed above.

As shown in Fig. 2, the metastable extended solubility C_s of the RE metals in silver-rich Ag–RE alloys decreases linearly with increasing difference in atomic radii $r_{RE} - r_{Ag}$. In other words, C_s increases as the lanthanide contraction $(r_{La} - r_{RE})$ increases.

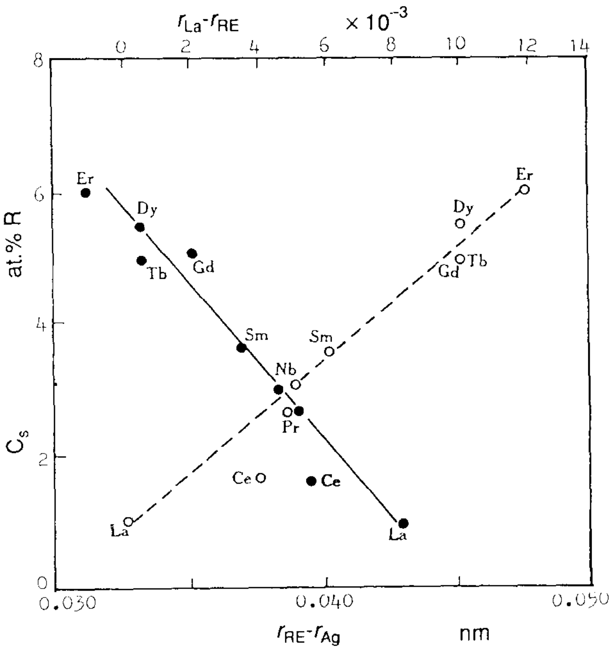

Fig. 2. C_s *vs.* $(r_{RE}-r_{Ag})$ and $(r_{La}-r_{RE})$ for Ag–RE alloys.

4.3. Influence of electron density in the Seitz atom cell

The large positive heat of mixing of liquid Ag–M (M≡Fe, Co, Ni, Cr, Mn) alloys implies a strong repulsion between solvent and solute atoms so that there is a miscibility gap in the liquid Ag–M alloy system and the extension of the solid solubility is restricted.

A surface tension theory of the solubility of a gas in a liquid can be used to explain the solubility C_l at the monotectic temperature and the metastable extended solid solubility C_s for Ag–M monotectic systems. According to the theory [14], the solubility can be written as

$$\ln C=\frac{-4\pi r^2\sigma E}{RT} \qquad (1)$$

Here, r is the atomic radius of the solute, σ is the surface tension and E is the interaction energy between the solvent and solute. Because the interaction energy between the gas solute and the liquid solvent is very small and the surface tension of the solute molecules is negligible, a conclusion can be drawn: the solubility, as in ln C above, of the gas solute in the liquid solvent is inversely proportional to the surface tension of the solvent. A similar conclusion was obtained by Chen and Zhang [15] for the solubility of a molten salt in a liquid metal. Obviously, the solubility of alloy elements in the liquid and solid states is more complicated, because the surface energy of the solute and the interaction energy between the solute and solvent cannot be neglected. For the monotectic system of silver with iron, cobalt, nickel, chromium or manganese, however, the E value in formula (1) is very small owing to the strong tendency towards repulsion and segregation between the two constituents. Considering the effect of the surface energy of the solute, we can infer from formula (1) that ln C_l or ln C_s should be inversely proportional to the ratio of or difference between the surface tension values of the solvent and solute. According to the theory offered by Miedema and Boom [16, 17], the surface tension (surface energy) of a liquid or solid metal is directly proportional to the electron density $n_{ws}^{1/3}$ in the Seitz atomic cell. Therefore the solubility ln C_l or ln C_s should be inversely proportional to $(n_{ws}^{1/3})_m/(n_{ws}^{1/3})_{Ag}$, where M is the solute. The electron density parameters $n_{ws}^{1/3}$ for silver and the alloying elements are taken from ref. 18. Figure 3 shows that such a relation exists in these alloy systems.

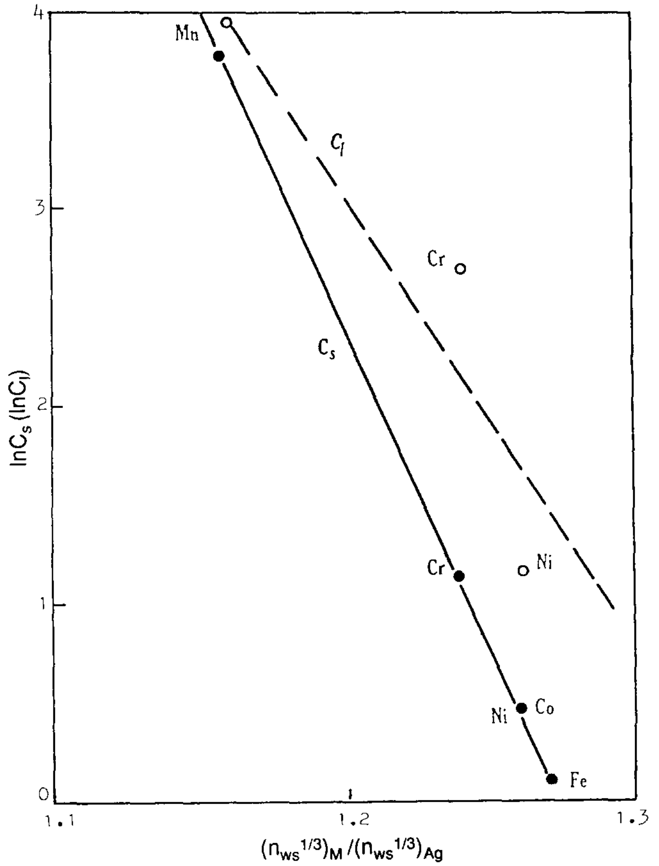

Fig. 3. Ln C_l or ln C_s *vs.* $(n_{ws}^{1/3})_M/(n_{ws}^{1/3})_{Ag}$ for Ag–M alloys (M≡Fe, Co, Ni, Cr, Mn).

5. Relationship between the extension of the solid solubility and the phase diagram

5.1. The alloy systems with negative heat of mixing

α(A)–A_mB_n eutectic systems are typical of this case; here α(A) is a terminal solid solution based on A and A_mB_n is a congruent compound. The Ag–Re and Ag–Zr systems studied in the present paper belong to this sort of eutectic system. The large negative heat of mixing of the liquid alloys and the large negative heat of formation of the stable solid compounds A_mB_n imply a strong mutual attraction between the two components, which may cause the formation of A_mB_n atomic clusters or seeds in the melt. The extension of the solid solubility is controlled by the crystallization rate and the fraction of A_mB_n crystals in the melt. A low crystallization rate and a small fraction of A_mB_n crystals is favourable to an extension of the solid solubility under rapid solidification. The ratio of the concentration branches $J=(C_m-C_{eu})/(C_{eu}-C_{eq})$ expresses the ratio of the α(A) crystal fraction to the A_mB_n crystal fraction at the eutectic point. Here C_{eu} is the solute concentration at the eutectic point and $C_m=n/(m+n)$, the solute concentration in the compound A_mB_n (see Fig. 4(a)). Obviously, the larger the J value is, the easier it is to prevent the crystallization of A_mB_n from the melt. This could cause a larger and even hypereutectic solid solubility extension. The extension parameter C_s/C_{eu}, the ratio of the extended solid solubility to the eutectic concentration, is directly proportional to the parameter J for the silver alloys studied in the present work and others, as shown in Fig. 5. The values of the extended solid solubility of aluminium alloys are taken from refs. 4 and 19. It can be seen from Fig. 5 that there is a hypereutectic extension ($C_s>C_{eu}$) when $J>10$, and there is a hypoeutectic extension ($C_s<C_{eu}$) when $J<10$. So the trend in the metastable extension of the solid solubility can be predicted from the appropriate eutectic phase diagram.

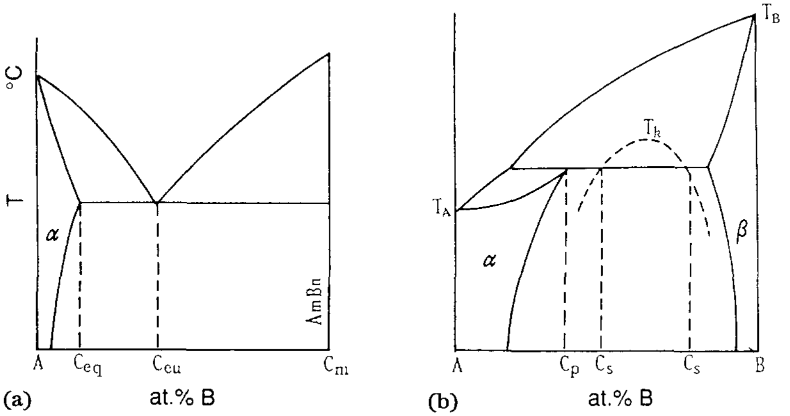

Fig. 4. Diagrammatic sketch of (a) α(A)$-A_mB_n$ eutectic system and (b) peritectic system.

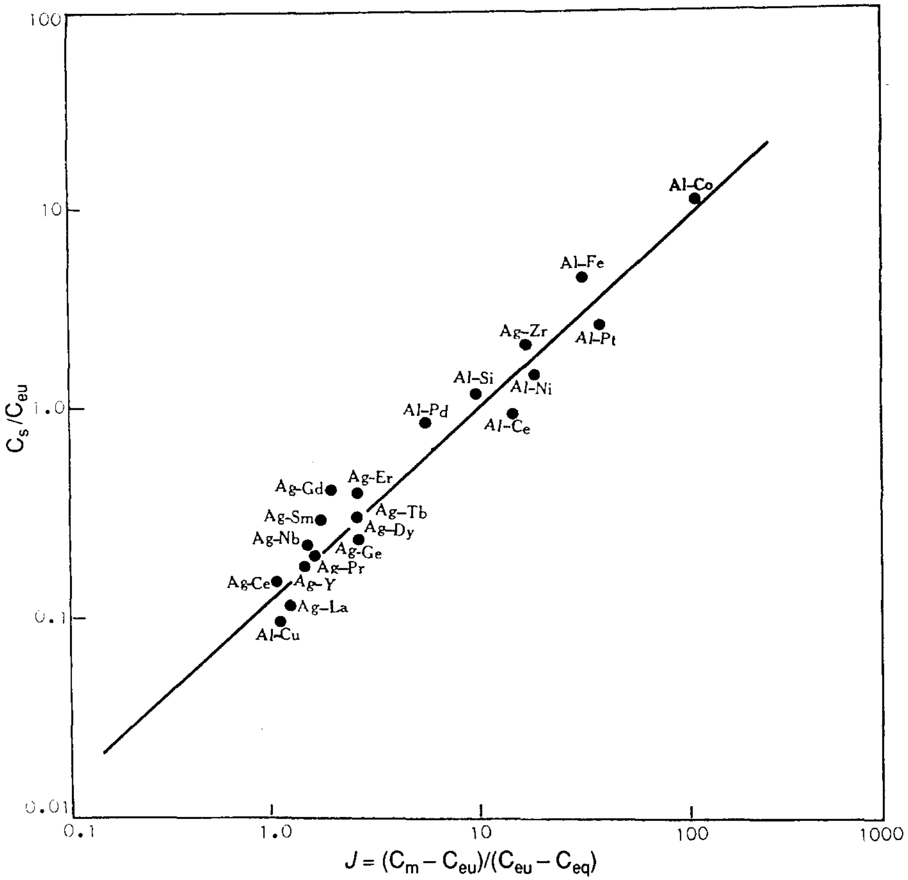

Fig. 5. Extension parameter C_s/C_{eu} *vs.* eutectic ratio of concentration branches J for silver and aluminium alloys.

5.2. The alloy systems with positive heat of mixing

The peritectic, monotectic and some simple eutectic systems belong to these sorts of systems, in which a strong mutual repulsion occurs between solute and solvent, and there are no A_mB_n-like clusters in the liquid alloys. Instead, there is a miscibility gap in the cooled melt range for peritectic and simple eutectic systems, and in the liquid alloy for monotectic systems [20]. The critical concentration C where the gap occurs is about 0.5, and the critical temperature is

$$T_k = \frac{2\Delta H_M}{(R+2\Delta S_m^x)} \quad [21]$$

In this case the extension of the solid solubility is restricted by the boundary line of the miscibility gap. The metastable extended solid solubility limit corresponds to the concentration at which the boundary line of the gap intersects the solidus, as shown in Fig. 4(b). The metastable extended solid solubility of Cu–Co alloys reported by Klement [22] is in accord with the solute concentration at the intersection point between the solidus and the boundary of the miscible region as determined by Nakagawa [20].

For monotectic systems, such as Ag–M ($M \equiv Fe$, Co, Ni, Cr, Mn) alloys, the boundary lines of the miscibility gap in the cooled melt should be projections of the line from the liquid. The measured C_s values (see Table 3) are each in accord with the solute concentration at the intersection point of the projected boundary line with the solidus.

The heat of mixing is positive in some simple eutectic systems, and a miscibility gap may also exist in the liquid or the cooled melt. For example, the critical temperatures T_k of the miscibility gaps in the Ag–Cu and Sn–Zn systems are 820 and 500 K [21] respectively. In the Sn–Zn system T_k is higher than the eutectic temperature T_{eu} (471 K), and the extension of the solid solubility is hypoeutectic ($C_s/C_{eu}=0.2$). In the Ag–Cu system with $T_k < T_{eu}$ (1052 K), the boundary line of the miscibility gap is under the solidus; a complete extension, or a continuous series of solid solutions is obtained.

Thus the size of the extension of the solid solution is related to the position and the trend of the boundary line of the miscibility gap. The solute concentration corresponding to the intersection point of the boundary line with the solidus is the limit of metastable extended solid solubility under melt quenching. If the boundary line is under the solidus, the extension can be complete.

In the peritectic phase diagram, if the melting point T_B of the solute B is higher than T_A, that of the solvent A, the liquidus of the terminal solid solution α(A) rises above T_A (Fig. 4(b)). However, the equilibrium solid solubility of such a peritectic system equals the concentration at the peritectic point, *i.e.* $C_{eq}=C_p$, and the extension of the α(A) solid solution must be beyond the peritectic point, *i.e.* $C_s/C_p > 1$. However, for the terminal solid solution β(B), since $T_A/T_B < 1$, the extended solid solubility of β(B) must be lower than the concentration at the peritectic point owing to the restriction of the immiscible region boundary line, *i.e* $C_s/C_p < 1$. So the extension parameter C_s/C_p for the peritectic system is connected with the ratio of solute melting point to solvent melting point. Taking T_A and T_B as the melting points of the solvent and solute, the extension parameter C_s/C_p for a peritectic system increases with T_B/T_A, as shown in Fig. 6, where the values of C_s for various alloys were taken from the present work and from refs. 3, 4 and 14. The C_s values of some alloys show quite large differences in the literature, so we used the largest value to calculate C_s/C_p. Figure 6 shows that the alloys in which $T_B/T_A < 1$ have hypoperitectic extensions, *i.e.* $C_s < C_p$, and the alloys where $T_B/T_A > 1$ have hyperperitectic extensions, *i.e.* $C_s > C_p$.

6. Summary

(1) Melt spinning and arc-melt hammer–anvil techniques were used to make ribbon and foil samples with a cooling rate of 10^6 K s^{-1}. The metastable

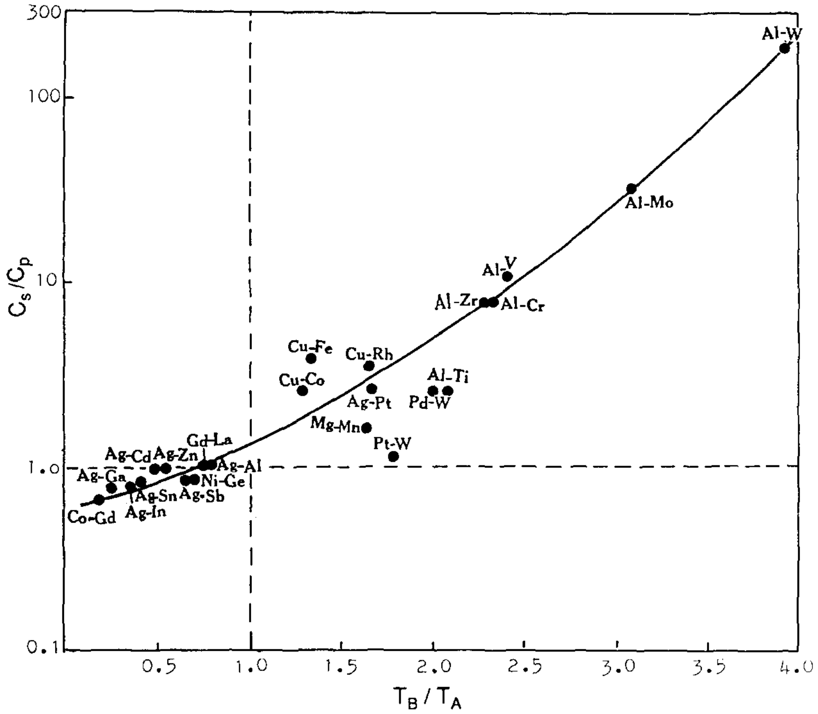

Fig. 6. Extension parameter C_s/C_p *vs.* T_B/T_A for peritectic systems: T_B, melting point of solute; T_A, melting point of solvent.

extended solid solubility of simple metals (aluminium, bismuth, cadmium, gallium, germanium, indium, lead, antimony, tin and zinc), transition metals (zirconium, iron, cobalt, nickel, chromium and manganese) and rare earth elements (yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium and erbium) in silver were measured using the lattice parameter method and are reported in this paper.

(2) Some factors influencing the extension of the solid solubility of these elements in silver were noted.

(i) Electron concentration rule: for alloy systems of silver and simple metals (such as aluminium, cadmium, indium, tin and zinc) with a peritectic reaction, the metastable extended solid solubility C_s is in accord with the electron concentration rule, namely the C_s values reach or closely approach the solute concentration corresponding to the electron concentration $e/a = 1.4$. The formation of the first electron compound ($e/a = 1.5$) in this sort of system limits the further extension of the solid solubility. The extended solid solubility of the eutectic Ag–Ge alloy reaches the concentration where $e/a = 1.4$ because the h.c.p. metastable intermediate phase Ag_5Ge, in which $e/a = 1.5$, is formed in the rapidly solidified alloy. The small size of the extension of the solid solubility of bismuth and lead in silver is due to the large difference in their atomic sizes.

(ii) Effect of atomic size: the metastable extended solid solubilities of rare earth elements in silver decrease linearly with increasing difference between the atomic radii of the solutes and the solvent, or alternatively increase linearly with the increasing lanthanide contraction from lanthanum to erbium.

(iii) The solid solubilities of the transition metals iron, cobalt, nickel, chromium and manganese in silver are also extended. The solubilities C_l of these solutes in liquid silver at monotectic temperatures and the metastable extended solid solubilities C_s are inversely proportional to the ratio of their electron densities in the Seitz atomic cell $(n_{ws}{}^{1/3})_M/(n_{ws}{}^{1/3})_{Ag}$.

(3) The relationship between the metastable extension of the solid solubility and the phase diagram has been discussed and some empirical rules have been proposed for eutectic, peritectic and monotectic systems. These empirical rules can be used to infer or predict the possibility and limits of solid solubility extension.

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References

1 G. Falkenhagen and W. Hofmann, *Z. Metallkd.*, *43* (1952) 69.

2 P. Duwez, R. H. Willens and W. Klement, Jr., *J. Appl. Phys.*, *31* (1960) 1136.

3 T. R. Anantharaman and C. Suryanarayana, *J. Mater. Sci.*, *6* (1971) 1111.

4 T. R. Anantharaman, P. Ramachandrarao, C. Suryanarayana, S. Lele and K. Chattopadhyay, *Trans. Indian Inst. Met.*, *30* (1977) 423.

5 H. Jones, *J. Mater. Sci.*, *19* (1984) 1043.

6 M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, pp. 1–57.

7 R. P. Elliot, *Constitution of Binary Alloys, First Supplement*, McGraw-Hill, New York, 1965, pp. 1–22.

8 W. B. Pearson, *A Handbook of Lattice Spacings and Structure of Metals and Alloys*, Pergamon, London, 1958, pp. 259–308.

9 He Chunxiao, Ma Guangchen, Wang Wenna, Wang Yongli and Zhao Huaizhi, *Phase Diagrams of Precious Metal Alloys*, The Metallurgical Industry Press, China, 1983.

10 K. A. Gschneidner, Jr., O. D. Mcmasters, D. G. Alexander and R. F. Venteicher, *Metall. Trans.*, *1* (1970) 1961.

11 G. Kjessler, D. Gebhardt and S. Steeb, *J. Less-Common Met.*, *26* (1972) 295.

12 R. Boom, F. R. de Boer and A. R. Miedema, *J. Less-Common Met.*, *45* (1976) 237; *46* (1976) 271.

13 P. Duwez, *ASM Trans. Q.*, *60* (1967) 607.

14 H. H. Uhlig, *J. Phys. Chem.*, *41* (1937) 1215.

15 Chen Nianyi and Zhang Guachen, *Kexue Tongbao*, *3* (1963) 68 (in Chinese).

16 A. R. Miedema and R. Boom, *Z. Metallkd.*, *69* (1978) 183.

17 A. R. Miedema and R. Boom, *Z. Metallkd.*, *69* (1978) 287.
18 A. R. Miedema, R. Boom and F. R. de Boer, *J. Less-Common Met.*, *41* (1975) 283.
19 H. Jones, *Aluminium*, *54* (1978) 274.
20 Y. Nakagawa, *Acta Metall.*, *6* (1958) 704.
21 B. Predel, *Acta Metall.*, *14* (1966) 209.
22 W. Klement, Jr., *Trans. Metall. Soc. AIME*, *227* (1963) 965.