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Glass forming ranges of cobalt-base thin film alloys

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The glass forming ranges of cobalt-base binary and ternary thin film alloys containing zirconium, titanium, niobium, molybdenum, vanadium and silicon have been studied in the cobalt-rich region. The minimum solute concentration for glass formation decreased with increasing difference in atomic radii or Pauling's electronegativity, as well as the cooling rate. Cobalt-base binary alloys readily showing glass formation are shown on the glass formation diagram. The values of atomic size effect in alloys sputtered at room temperature were about 0.065, and decreased with increase of cooling rate. The value was decreased in alloys having a large heat of formation. In ternary cobalt alloys containing zirconium, niobium, molybdenum and vanadium, the glass forming range could not be interpreted as the concept of atomic size effect alone.

1. Introduction

A number of cobalt-base amorphous thin film alloys containing transition metals have been prepared by sputtering and investigated extensively, because these alloys are highly attractive as soft magnetic materials [1, 2]. To produce a stable amorphous phase, it is important to know the glass forming ability (GFA) which is related to alloy composition and cooling condition. Until now, a major part of the GFA studies was mainly concentrated on alloys made by liquid quenching and those of thin film alloys were very limited, because the estimation of cooling rate was very difficult in the case of sputtering. Among the several parameters used to discuss the GFA, atomic radii difference was frequently used for thin film alloys [3, 4] and electronegativity difference and valence difference were also used [3]. The minimum solute concentration required to produce the amorphous phase was decreased with increasing difference in atomic radii, electronegativity and valence in iron-base thin film alloys [3]. In the case of the cobalt-early transition metal (ETM) system, the same dependence of solute limit on atomic radii difference was reported by Fukamichi and Shimada [5] but other parameters were not discussed. Recently, Ueno and Waseda [6] suggested that the concept of atomic size effect, defined as the product of the volume mismatch term and the minimum solute concentration for glass formation, could be used to interpret the GFA in many alloy systems. They reported that the atomic size effect, λ_0, was 0.10 regardless of the difference of quenching technique. But the difference in cooling rate can change the minimum solute concentration [7], thus it was considered that the atomic size effect should be corrected if a more rapid quenching technique, such as sputtering, was used to make amorphous alloys.

In this work, the glass forming ranges of some cobalt-base thin film binary alloys such as Co–Zr, Co–Ti, Co–Nb, Co–Mo, Co–Si and ternary alloys such as Co–Zr–Mo, Co–Zr–Nb and Co–Zr–V are studied in the cobalt-rich side. The glass forming ranges are discussed in terms of several parameters such as atomic size factor, electronegativity and thermodynamic factor. The concept of atomic size effect suggested by Ueno and Waseda is used to discuss the minimum solute concentration for glass formation.

2. Experimental procedure

Thin film alloys were made using an r.f. magnetron-type sputtering apparatus. The target consisted of a pure cobalt plate of 6 in. diameter, and small plates of corresponding metal. The substrate was a polyimide film of 10 in. diameter. The sputtering was carried out at an argon pressure of 10 mtorr and the input power of 300 W for 1 h. The substrate temperature was 300 K for all alloys and the temperature of 400 K was selected to determine the effect of cooling condition for the Co–Zr system.

To obtain a compositional profile on a substrate, the concentration spread mode was undertaken by non-uniform disposition of metal plates on a cobalt-target without substrate rotation for binary and ternary alloys. The formation of amorphous phase was determined by X-ray diffractometer, and the chemical composition was analysed using an energy dispersive X-ray spectrometer (EDS) whose compositional scattering was ±0.3 at.% compared with the results of wet chemical analysis. The film thickness was measured using a scanning electron microscope

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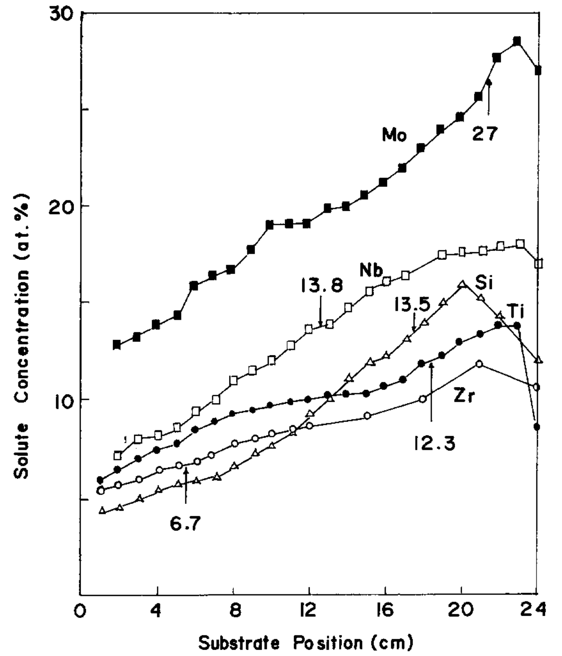

Figure 1 The compositional profiles of sputtered films relative to substrate position and the minimum solute concentrations for glass formation in cobalt–early transition metals (zirconium, titanium, niobium and molybdenum) and Co–Si binary alloys.

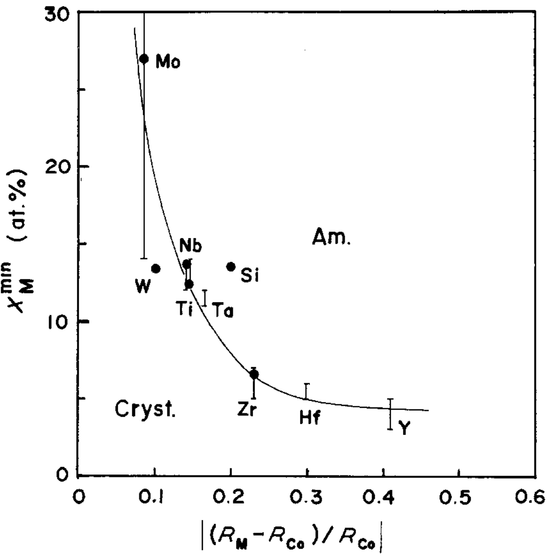

Figure 2 Dependence of minimum solute concentration, X_M^{min}, for glass formation on the atomic radii difference, $|R_M - R_{Co}/R_{Co}|$, between the constituent elements in Co–M alloys.

(SEM), and the thickness range was 500 to 600 nm. The cooling rate during sputtering was indirectly estimated from the columnar size comparison of a Co–Cr film made under the same sputtering conditions used for other measurements [8].

3. Results and discussion

3.1. Glass forming ranges of binary alloys

The compositional profiles of thin film Co–ETM (Zr, Ti, Nb and Mo) and Co–Si binary alloys at the substrate temperature of 300 K are shown in Fig. 1 relative to the substrate position, and the minimum solute concentrations for glass formation obtained by X-ray diffraction are indicated by arrows. The minimum solute concentrations are 6.7 at.% Zr, 12.3 at.% Ti, 13.8 at.% Nb and 27 at.% Mo for Co–Zr, Co–Ti, Co–Nb and Co–Mo thin film alloys, respectively. These values agree well with other results [5] for Co–Zr, Co–Ti and Co–Nb alloys, while that of Co–Mo alloy is located in the middle of other results [4, 9]. In Co–Si alloy produced to determine the effect of adding a metalloid element, the amorphous state was obtained at above 13.5 at.% Si.

TABLE I Atomic radius and Pauling's electronegativity of elements and the minimum solute concentrations for amorphous formation in cobalt binary thin film alloys from several sources

Element	Atomic radius (nm)	Pauling's electronegativity	Minimum solute concentration X_M^{min} (at.%)
Co	0.128	1.88	
Y	0.199	1.22	4 [5], 3–5 [10]
Ti	0.146	1.54	12.3, 12.5 [5], 14 [11]
Zr	0.158	1.33	6.7, 5 [5] 7 [1]
Hf	0.167	1.30	5 [10], 6 [5]
Nb	0.146	1.60	13.8, 12.5 [5], 12 [10]
Ta	0.149	1.50	11 [12], 12 [5]
Mo	0.139	2.16	27, 14 [9], 35 [4]
W	0.141	2.36	13 [13]
Si	0.102	1.90	13.5

To discuss the correlation between the parameters for the GFA and the minimum solute concentration (X_M^{min}) for glass formation in cobalt-base thin film alloys, X_M^{min} values from several sources, including these results, were collected and the atomic radii and Pauling's electronegativity of the constituent elements are given in Table I. In evaluating the atomic size factor for amorphous alloys, the selection of atomic radius is very important. Among several atomic radii, values of Table I were selected from those of Ueno and Waseda's work [6], because they determined it mainly from the experimental radial distribution function or the close packed metallic radius of the corresponding element. X_M^{min} from other sources were the measured values from samples made by r.f. sputtering at room temperature, corresponding to the similar experimental conditions in this work.

The minimum solute concentrations are shown in Fig. 2 as a function of the atomic radii difference of metals listed in Table I. It is seen that the amorphous cobalt alloys can be made at lower concentrations of added elements with large atomic radii difference, but become unstable when approaching to the same atomic size as that of the cobalt atom. In this figure it can be seen that X_M^{min} smoothly decreases with increasing atomic size difference, though Fukamichi *et al.* [5] suggested that the relation has a linearity in cobalt-rich alloys. This demonstrates that a large difference in atomic size between cobalt and the alloying elements is one of the most important factors in obtaining the cobalt-rich amorphous alloys by the sputtering technique.

Fig. 3 shows the relation between X_M^{min} and Pauling's electronegativity difference between cobalt and the solute elements known as one parameter for interpreting the GFA. Although X_M^{min} roughly decreases with increasing electronegativity difference, the data of cobalt alloys including molybdenum, silicon and tungsten are largely scattered. Therefore, it is considered

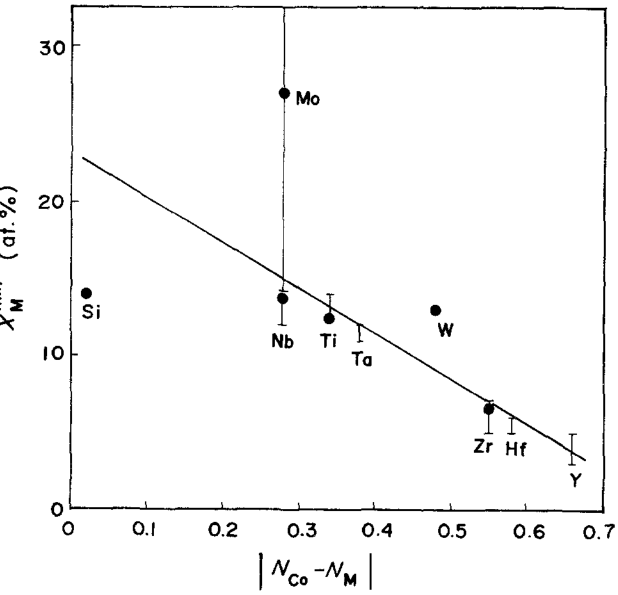

Figure 3 Dependence of the minimum solute concentration, X_M^{min}, for glass formation on Pauling's electronegativity difference, $|N_{Co} - N_M|$, between the constituent elements in Co–M alloys.

that the electronegativity difference is a crude parameter in interpreting the GFA.

As an approach to predict the glass forming range, a glass formation diagram was suggested by Giessen [14] and Whang [15]. In their diagrams the range showing ready glass formation (RGF) is located in the lower left quadrant of the *H–R* plot or *T–C* plot. Fig. 4 shows the glass forming map in the cobalt-base system constructed using the approach suggested by Whang [15]. In this map, T_{LR} and C_{er} were calculated from the phase diagrams of corresponding alloys using Whang's definition. Solid and dashed lines represent the glass forming boundaries of sputtering and liquid quenching, respectively. Using this map, if a certain rapid quenching technique is chosen to make an amorphous cobalt alloy, the glass forming possibility can be predicted. It is seen that the glass forming systems by sputtering are expanded compared with that of liquid quenching, and the glass forming system is related to the quenching method.

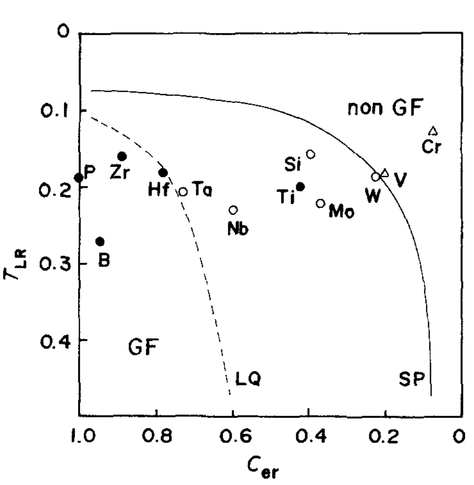

Figure 4 The reduced temperature, T_{LR}, plotted against the relative composition ratio, C_{er}, for Co–M alloys. (○) and (●) represent the glass forming alloys in sputtering and liquid quenching, respectively, and (△) represents the non-glass forming alloys by both methods.

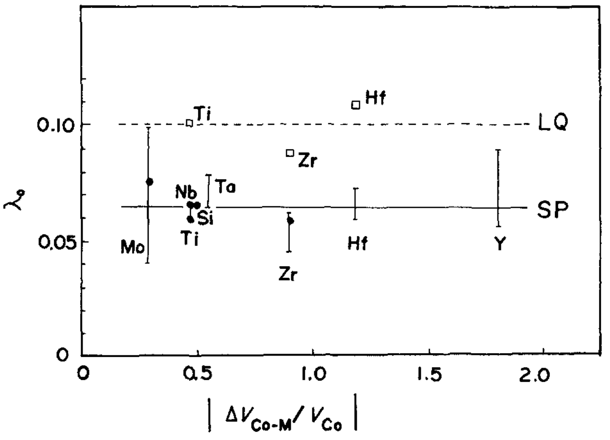

Figure 5 Relation between the atomic size effect, λ_0, and the atomic volume mismatch, $|\Delta V_{Co\text{-}M}/V_{Co}|$, for Co–M alloys. (——) Sputtering and (– – –) liquid quenching results.

Recently, Ueno and Waseda [6] reported that the conditions for glass formation in alloy A–B could be determined by the simple term, the atomic size effect (λ_0), alone. They defined λ_0 as

$$\lambda_0 = |\Delta V_{AB}/V_A| X_B^{min} \tag{1}$$

$$\Delta V_{AB}/V_A = (R_B/R_A)^3 - 1 \tag{2}$$

where X_B^{min} is the minimum solute concentration of B required to form amorphous phase and $\Delta V_{AB}/V_A$ is the volume mismatch. ΔV_{AB} and V_A are the volume difference between the cubes of the constituent atoms A–B and the volume of the cube of A atom, respectively. They reported that λ_0 had a constant value of about 0.10 for many binary alloys regardless of rapid quenching technique. To see the availability of their concept in the case of sputtering, the values of λ_0 were calculated using the results of Table I and represented as a function of the atomic volume mismatch in Fig. 5. In this figure the λ_0 values on liquid quenching were calculated from the results of X_M^{min} of Co–Zr [16], Co–Hf [17], Co–Ti [18] and Co–B [19] alloys reported by several workers. All data for cobalt-base thin film alloys scatter around $\lambda_0 \simeq 0.065$, while those of liquid quenching locate at about $\lambda_0 \simeq 0.10$, suggested by Ueno and Waseda [6]. This demonstrates that the atomic size effect is related to the cooling condition.

Generally, the cooling rate in sputtering is considered to be about 10^8 K sec^{-1} [20], but the cooling rate during sputtering is changed with the sputtering conditions such as substrate temperature and input power. To see the effect of cooling conditions during sputtering, thin film samples were made at the substrate temperature of 400 K for the Co–Zr system. X_M^{min} was determined with the same manner of Fig. 1. The cooling rate during sputtering was indirectly estimated according to a comparison of columnar size in Co–20 wt % Cr film made under the same sputtering conditions as used previously [8], Co–Cr film being selected for this investigation. The results of X_M^{min} at 400 K are given in Table II together with other results of Co–Zr obtained from the facing target sputtering technique [21] and liquid quenching [16]. Although the cooling rate was indirectly estimated, the results show that X_M^{min} can be decreased with increasing cooling

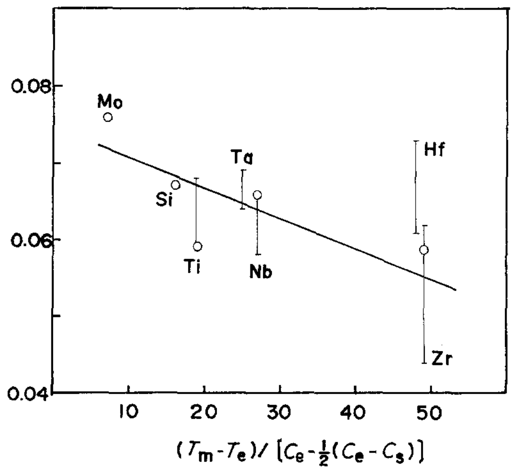

Figure 6 Relation between the atomic size effect, λ_0, and the slopes of temperature and composition, $(T_m - T_e)/[C_e - 1/2(C_e - C_s)]$, estimated from the phase diagrams for Co–M thin film alloys.

rate. Because the atomic size effect is a function of X_M^{min}, it can be seen that λ_0 is not a constant but a variable related to the cooling rate and decreases with increasing cooling rate. This trend was also satisfied in metal–metalloid systems such as Fe–B and Fe–P alloys [22].

Although the amorphous forming tendency is primarily related to the size factor between the constituent elements, the scattering of λ_0 in the alloy system in Fig. 5 considered due to other factors such as chemical affinity. In crystalline materials, alloys having a strong chemical bond strength largely contract in volume during solidification [23] and this will also occur in amorphous alloys.

Fig. 6 shows the relation between the atomic size effect and the slope, $(T_m - T_e)/(C_e - 1/2(C_e - C_s))$, of temperature difference to concentration difference obtained from the cobalt-rich side of the corresponding alloy phase diagram. T_m, T_e,C_e and C_s are the melting point of cobalt, the eutectic temperature, the eutectic concentration and the solute limit of solid solution at the eutectic temperature, respectively. With increase in the slope of dT/dc, λ_0 approximately decreases. Large values of dT/dc implies a large chemical affinity between the constituent elements. Therefore, it is considered that the atomic size effect necessary to form the amorphous phase can be decreased in alloy systems having a large chemical affinity.

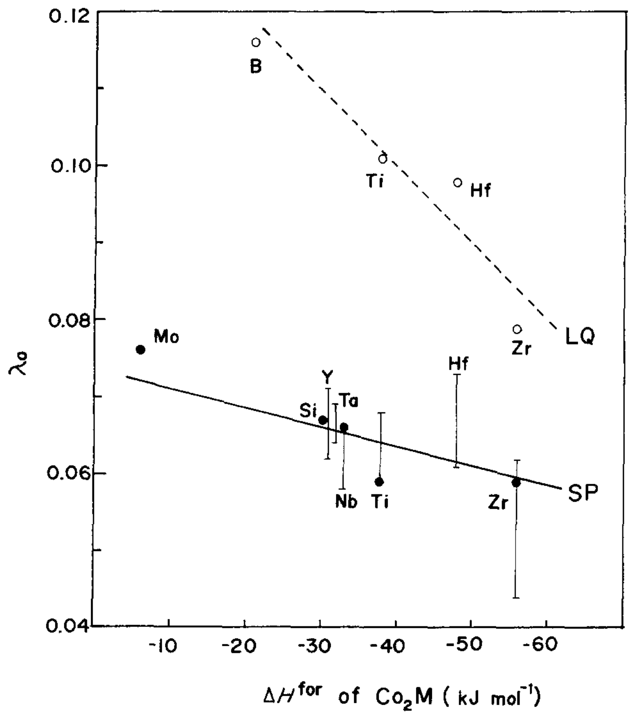

Figure 7 Relation between the atomic size effect, λ_0, and the heat of formation, ΔH^{for}, of Co_2M compound in Co–M alloys. (——) Sputtering and (– – –) liquid quenching results.

It is well-known that chemical affinity influences the glass forming ability [14], but the quantitative parameter expressing this chemical affinity has not yet been revealed. In this work, the concept of heat of formation, which is considered as a crude parameter, was examined. From phase diagrams of cobalt–early transition metal systems, it is seen that the Co_2M-type intermetallic compound is very stable. In the study of amorphous structure of Fe–Zr [24], it was considered that Fe_2Zr compound was similar to an amorphous structure. Assuming that Co_2M type is similar to the amorphous structure in cobalt-rich alloys, the heat of formation of Co_2M compound can be calculated from the Miedema model [25].

TABLE II The minimum solute concentration, X_{Zr}^{min}, for glass formation, the atomic size effect, λ_0, the substrate temperature, the columnar size of Co–Cr under nearly the same sputtering conditions, and the estimated cooling rate for Co–Zr alloy

X_{Zr}^{min}	λ_0	Substrate temperature (K)	Columnar size of Co–Cr (μm)	Estimated cooling rate (K sec^{-1})
7.5	0.066	400	0.2	$\sim 10^7$
6.7	0.059	300	0.07	$\sim 10^8$
2*	0.018	300	0.03	$\sim 10^9$
9	0.079	Liquid quenching		$\sim 10^6$

*Measured value [21] from sample made by the facing target sputtering method in which the substrate heating effect is very small.

Fig. 7 shows the relation between the atomic size effect, λ_0, and the heat of formation in cobalt-base alloys made by sputtering and liquid quenching. In this figure λ_0 decreases linearly with increasing heat of formation, ΔH^{for}, of Co_2M in both cases of sputtering and liquid quenching. Thus, the amorphous phase can easily be obtained in alloys having a large negative heat of formation at the same cooling rates.

In conclusion, although the concept of atomic size effect is simple and available for interpreting the GFA, it is thought that the effects of cooling rate of the quenching method used and the chemical affinity between the constituent elements, must be considered in order to predict the glass forming range.

3.2. Glass forming ranges of ternary alloys

Fig. 8 shows the glass forming boundaries on the cobalt-rich side for Co–Zr–Nb, Co–Zr–Mo and Co–Zr–V ternary alloys in sputtering and for Co–Zr–Mo and Co–Zr–V alloys in liquid quenching [26]. The glass forming ranges in sputtering are wider than those of liquid quenching in Co–Zr–Mo and Co–Zr–V systems because of the difference in cooling rate. The

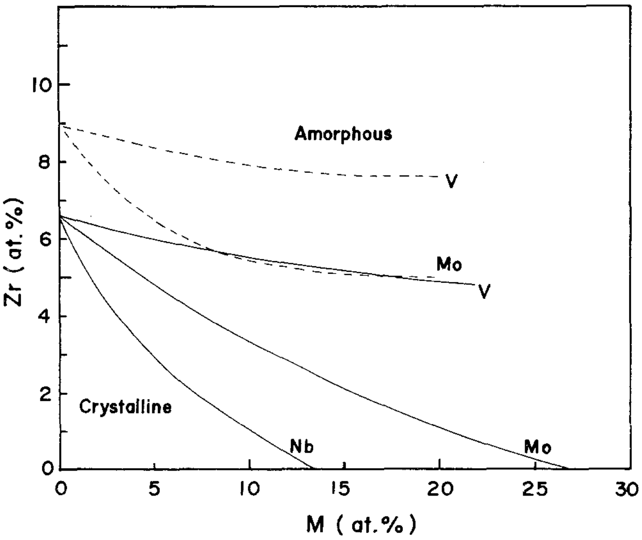

Figure 8 Glass forming ranges of Co–Zr–M (M = Nb, Mo and V) ternary alloys. (——) Sputtering and (– – –) liquid quenching results.

glass forming range in sputtering is increased in the order Co–Zr–V, Co–Zr–Mo and Co–Zr–Nb alloys. This order corresponds to the magnitude of atomic radii difference between the base and the third element. In addition, the minimum solute concentration for glass formation in ternary alloy is primarily related to the atomic size factor and decreases with increasing atomic radii difference between the base and third elements. In this figure the glass forming range of the Co–Zr–Nb system shows a deep concave line, while that of the Co–Zr–V system is almostly straight, and that of Co–Zr–Mo falls between the other two systems. The difference cannot be interpreted only by the atomic size difference term because the glass forming boundary must show a straight line if the atomic size difference only influences the glass forming ability. Thus, the deviation from the straight line connecting the minimum solute concentration of binary alloys must be considered due to another effect, such as chemical bonding characteristics between the constituent elements. Discussion of this was not undertaken in this work because of insufficient data relating to cobalt ternary alloys.

To discuss the atomic size effect, λ_0', in ternary alloy, λ_0' values were calculated using data of Fig. 8 in the following equation suggested by Ueno and Waseda [6], and as shown in Fig. 9.

$$\lambda_0' = |\Delta V_{AB}/V_A| X_B + |\Delta V_{AC}/V_A| \cdot X_C^{\min} \qquad (3)$$

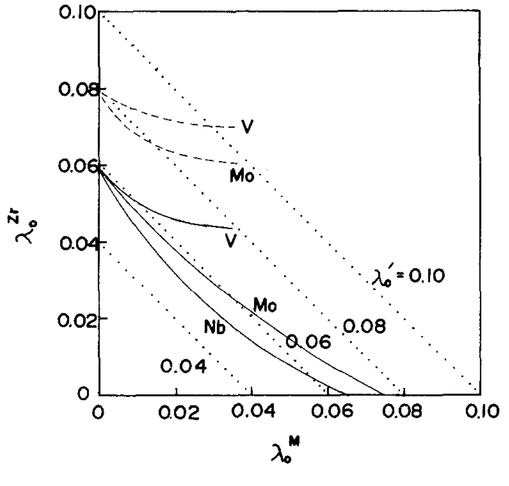

Figure 9 The ranges of atomic size effect, λ_0', for Co–Zr–M ternary alloys (M = Nb, Mo and V). (——) Sputtering and (· · ·) liquid quenching results.

The tendency of λ_0' is similar to that of Fig. 8. In this figure, the λ'_0 lines of Co–Zr–Nb and Co–Zr–Mo systems are located in the range of $\lambda_0' = 0.05$ to 0.075 and that of Co–Zr–V is largely deviated with increasing vanadium content. The value of λ_0' in the Co–Zr–Nb system was lowered to about 0.05. Therefore, for cobalt–early transition metal ternary systems, it is seen that the concept of atomic size effect is difficult to apply in order to discuss the GFA.

4. Conclusion

The glass forming ranges of cobalt-base binary and ternary thin film alloys made by r.f. magnetron sputtering were studied in terms of atomic radius, Pauling's electronegativity and thermodynamic factor. The minimum solute concentration required to form an amorphous phase decreased with increasing difference in atomic radii or Pauling's electronegativity between the constituent elements, and increased in the lower cooling rate due to increase of the substrate temperature. By constructing a glass formation diagram, represented as the relation of the reduced temperature and the relative compositional ratio, binary cobalt alloys showing ready glass formation were suggested in the case of sputtering. The values of atomic size effect in thin film alloys sputtered at room temperature were about 0.065 and this value increased with decreasing cooling rate. The difference in atomic size effects on the alloy system was discussed as the dependence of temperature on composition estimated from the phase diagram on the cobalt-rich side and the difference in the heat of formation of Co_2M compound. The value of atomic size effect decreased with increasing heat of formation between the constituent elements. The concept of atomic size effect should not be used to interpret the glass forming range in cobalt–early transition metal ternary alloys such as Co–Zr–V and Co–Zr–Mo systems.

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