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The influence of compound-forming tendency on Al-based-glass formability

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Abstract

The effects of some metals (they include Fe, Ni, Cu, Zn and can be regarded as 'honorary' transition metals; here these metals are referred to as 'TM') and Ce on the microstructures of Al–TM–Ce amorphous alloys have been studied by means of x-ray diffraction and differential scanning calorimetry experiments. The prepeak positions of Al₉₀Fe₅Ce₅, Al₉₀Ni₅Ce₅, Al₉₀Cu₅Ce₅ and Al₈₃Zn₁₀Ce₇ amorphous alloys shift to smaller angles with increasing atomic number of the TM. The Al–Zn–Ce amorphous alloy was first obtained by adding Ce to improve the compound-forming tendency and prevent phase separation. The crystallization temperatures and crystallization activation energies of Al₉₀Fe₅Ce₅, Al₉₀Ni₅Ce₅, Al₉₀Cu₅Ce₅ and Al₈₃Zn₁₀Ce₇ amorphous alloys decrease gradually. The intensity of the interaction between atoms, W , determined by the atomic radius and the electronegativity, can qualitatively reflect the compound-forming tendency and the effects of elements on the glass formability. According to increasing W -value, we can arrange the TM elements in the following order: Mg, Mn, Zn, Cr, Cu, Ni, Fe. The glass formability and the compound-forming tendency of Al–TM–Ce alloys also increase in this order.

1. Introduction

Aluminium-based metallic glasses with remarkably high Al content have technological importance, especially in applications requiring high-strength low-density materials [1, 2]. This kind of metallic glass is far away from the eutectic region, and it fails to satisfy the atomic size criterion for glass formability [3], so it is quite different from the usual glass-forming systems. Past interest has been centred on the origin of Al-based-glass formability [4] and the chemical short-range order (CSRO) [5] in Al-based glasses. Several factors referred to as the alloy–chemical factors are known to be correlated with the ease of glass formation.

These include the atomic sizes of various elements composing the alloy, valence electron concentration and the heat of compound formation [6]. In the earlier studies, it was argued that the strong interaction between unlike atoms is correlated with the ease of Al-based-glass formation.

In our previous work [7, 8], a prepeak in the structure factor of an $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ melt which is at a similar position to the prepeak for an $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ amorphous alloy has been observed. From x-ray diffraction (XRD) and differential scanning calorimetry (DSC) experiments, it can be concluded that Al-based metallic glasses inherit the CSRO corresponding to the prepeak from the melt, which is favourable for Al-based-glass formation.

In an attempt to improve the stability and formability of Al-based metallic glasses, we report on the influence of transition metals (TM) and Ce on the microstructure, stability and compound-forming tendency (possibility and difficulty of compound formation) of Al-based glasses. On the basis of the experimental results, we propose that the interaction between atoms determined by the atomic radius and the electronegativity can qualitatively reflect compound-forming tendency and the effect of elements on glass formability.

2. Experimental procedure

Amorphous ribbons were obtained by the single-roller melt-spinning technique under a partial argon atmosphere. The diameter of the copper roller was 35 cm, with a typical circumferential velocity of 40 m s^{-1} . The quenched samples were investigated by using x-ray wide-angle scattering with a θ - θ diffractometer (2θ is the scattering angle) and Mo $\text{K}\alpha$ radiation. Small-angle x-ray scattering (SAXS) measurements were performed at room temperature using an apparatus with a $0.5 \text{ mm} \times 0.5 \text{ mm}$ point-focus Cu $\text{K}\alpha$ incident beam. Thermal analysis was carried out by using a Netzsch DSC-404 system under a pure argon atmosphere.

3. Results

XRD patterns of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ amorphous alloys are shown in figure 1. Prepeaks appear in the XRD curves. The positions of the main peaks remain constant, but the prepeak positions are shifted slightly. For the Al-TM-Ce alloy with Al content up to 90 at.% it is much easier to obtain the amorphous microstructure than for an $\text{Al}_{90}\text{TM}_{10}$ alloy. Some $\text{Al}_{90}\text{TM}_{10}$ alloys (such as $\text{Al}_{90}\text{Fe}_{10}$, $\text{Al}_{90}\text{Ni}_{10}$, $\text{Al}_{90}\text{Cu}_{10}$) have strong interactions between unlike atoms and strong compound-forming tendencies, so they are liable to form intermetallic compounds. Some $\text{Al}_{90}\text{TM}_{10}$ alloys (such as $\text{Al}_{90}\text{Zn}_{10}$, $\text{Al}_{90}\text{Pb}_{10}$) have weak interactions between unlike atoms [9, 10], so they are liable to exhibit phase separation. Therefore, the stability of the single phase for $\text{Al}_{90}\text{TM}_{10}$ is fairly weak. Upon adding Ce into Al-Fe, Al-Ni and Al-Cu alloys, glass formation becomes easier to achieve for these alloys.

In order to investigate the effects of the single-phase stability and Ce on Al-based-glass formability, the microstructures of Al-Zn-Ce quenched alloys have been studied. Figure 2 shows XRD patterns of $\text{Al}_{90}\text{Zn}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ quenched samples. The microstructure of the $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ quenched alloy is completely amorphous, and a prepeak is found at the scattering angle 2θ of 8.32° . The $\text{Al}_{90}\text{Zn}_5\text{Ce}_5$ quenched sample is found to contain the Al phase, an amorphous phase and some Al_2CeZn_2 intermetallic compound. As the concentrations of Zn and Ce increase, an intermetallic compound appears, which prevents the original phase from separating into Al and Zn phases, and improves the stability of the single

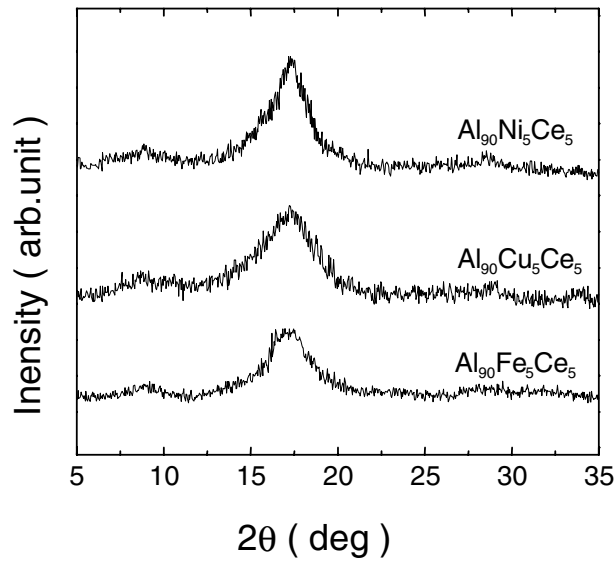


Figure 1. X-ray diffraction patterns of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ amorphous alloys.

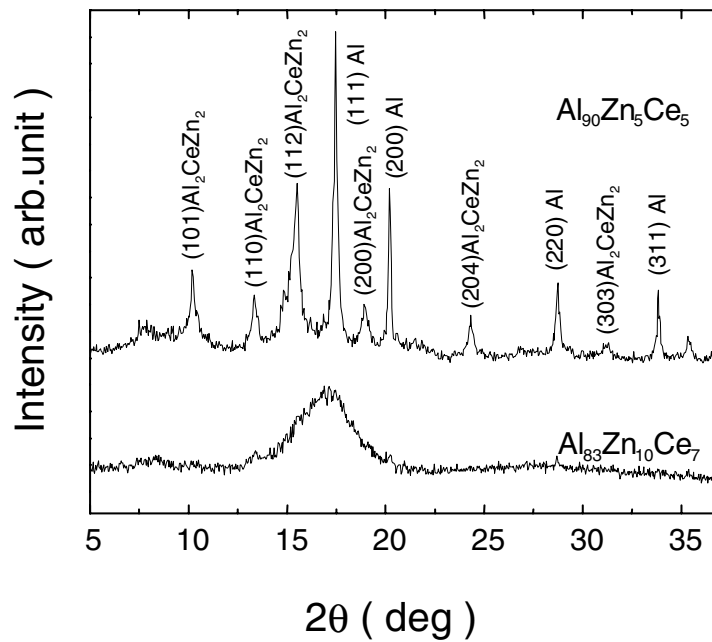


Figure 2. X-ray diffraction patterns of $\text{Al}_{90}\text{Zn}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ quenched specimens.

phase. Therefore, increase of the Zn and Ce concentrations is helpful as regards facilitation of Al-based-glass formation.

The prepeak caused by strong interaction between unlike atoms corresponds to a cluster structure with CSRO. The structural unit size corresponding to the prepeak may be estimated according to a formula [11]: $R = \lambda / (2 \sin \theta_{pp})$, where R is a characteristic distance related

to the structural unit size, λ is the wavelength of the Mo $K\alpha$ radiation and θ_{pp} is the scattering angle at the prepeak. The peak positions and structural unit sizes of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys are shown in table 1. The positions of the main peaks remain constant except for the $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ quenched alloy, but the prepeak positions are shifted slightly to smaller angles and the structural unit sizes corresponding to the prepeak increase with increasing atomic number of the TM. This is because of the increase of the atomic radius with the atomic number. TM elements affect the CSRO structure corresponding to the prepeak, but have no effect on the Al matrix corresponding to the main peak. The positions of the prepeak and the main peak of the $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloy shift to smaller angles because of the higher concentrations of Zn and Ce and the bigger atomic radii of Zn and Ce.

Table 1. The peak positions and structural unit sizes corresponding to the prepeaks of Al–TM–Ce amorphous alloys.

Al–TM–Ce	Main peak position 2θ (deg)	Prepeak position 2θ (deg)	Structural unit size R (nm)
$\text{Al}_{90}\text{Fe}_5\text{Ce}_5$	17.3	8.9	0.457
$\text{Al}_{90}\text{Ni}_5\text{Ce}_5$	17.3	8.8	0.462
$\text{Al}_{90}\text{Cu}_5\text{Ce}_5$	17.3	8.6	0.472
$\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$	17.1	8.3	0.489

In figure 3 we show DSC continuous heating curves for $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys. There are two exothermic peaks in the DSC curves. The weak exothermic peak at the lower temperature corresponds to the Al phase crystallization, and the peak at the higher temperature corresponds to the formation of the intermetallic compound. The second peaks in the DSC curves of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys are found at 348.2 °C, 326.3 °C, 270.8 °C and 214.4 °C, respectively. The crystallization activation energies at the second peaks of these four

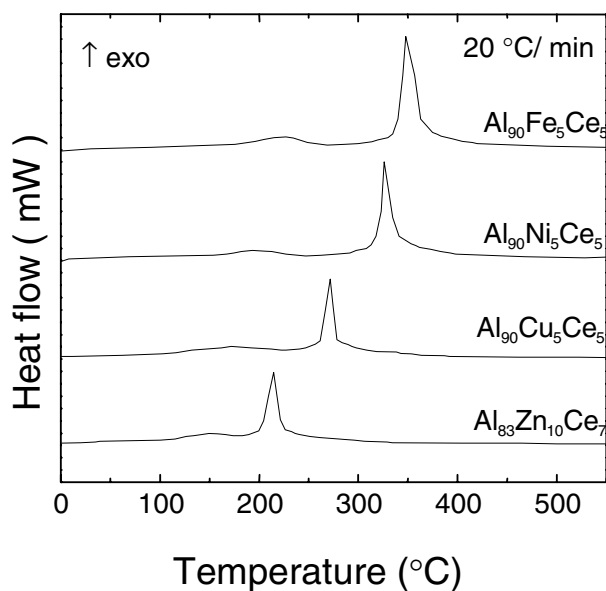


Figure 3. DSC curves of four Al–TM–Ce amorphous alloys.

alloys are 74.15 mJ mg^{-1} , 64.35 mJ mg^{-1} , 47.19 mJ mg^{-1} and 37.90 mJ mg^{-1} , respectively. The crystallization temperature and crystallization activation energy of amorphous Al–TM–Ce alloys decrease with increasing atomic number of the TM. This indicates that the stability of these amorphous alloys increases with decreasing atomic number of the TM.

In order to investigate the influence of the TM on the microstructure of Al–TM–Ce amorphous alloys, SAXS measurements were performed. Figure 4 shows SAXS results for $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys. Although these four alloys are all amorphous, there are differences between their SAXS curves. The scattering intensities for $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ alloys are relatively flat against the scattering angle, but the scattering intensities for $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ alloys are much steeper, which implies the existence of more obvious concentration fluctuations in $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys. The concentration fluctuation has the characteristics of the early stages of phase separation [12]. The SAXS results indicate that $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys are liable to undergo phase separation, and that for $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ amorphous alloys it is more difficult to produce phase separation. The occurrence of concentration fluctuations in Al-based glasses may be related to the interaction between unlike atoms.

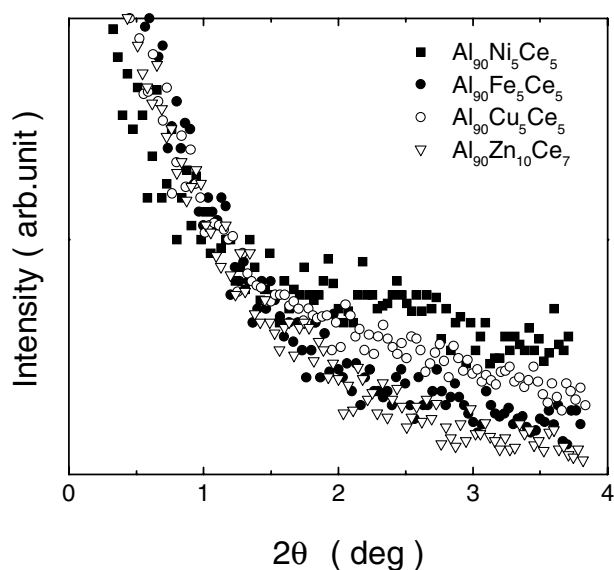


Figure 4. SAXS results for four Al–TM–Ce amorphous alloys.

4. Discussion

The compound formation is determined by the interaction between atoms and the atomic radius. The maximum solubility of a TM in an Al-based alloy corresponds to the minimum concentration of the TM for compound formation. The stability of the intermetallic compound increases with decreasing maximum solubility of the TM. Therefore, the compound-forming tendency can be qualitatively indicated by the maximum solubility of the TM. According to Hume-Rothery's theory [13] and the Darken–Gurry theory [14], the intensity of the interaction between atoms, W , may be estimated from the atomic radius difference $\varepsilon = (r_A - r_B)/r_A$

and the electronegativity difference $N = N_A - N_B$ (where A is the solvent atom and B is the solute atom), reflecting the compound-forming tendency and stability of Al-based alloys. The intensity of the interaction between the A atom and B atom is described as follows:

$$W_{AB} = (\varepsilon/0.15)^2 + (N/0.4)^2. \quad (1)$$

W_{AB} can be obtained in accordance with the atomic radius and electronegativity of the elements. The values of W for some Al alloys and TM–Ce alloys are as shown in table 2. Figure 5 shows the relation of the maximum solubility of the element in the Al alloy [15] and the W -value. In a certain range, the maximum solubility of the element (or the minimum concentration of the element for compound formation) decreases with increase of the W -value. The maximum solubilities of Fe and Ni in Al alloys are lower because of the strong Al–Fe and Al–Ni chemical bonds. The stability of the intermetallic compound increases and the compound-forming tendency becomes stronger with increasing W -value. This indicates that Darken–Gurry theory is suitable for analysing the compound-forming tendency of Al-based alloys.

Table 2. The intensity of the interaction between relevant elements.

Element A	Element B	ε (%)	ε_r	N_{AB}	N_r	W
Al	Fe	13.29	0.8858	−0.3	−0.75	1.347
	Ni	12.59	0.8392	−0.3	−0.75	1.267
	Cu	10.49	0.6993	−0.4	−1.00	1.489
	Zn	6.993	0.4662	−0.1	−0.25	0.2798
	Ce	−27.97	−1.865	0.4	1.00	4.478
	Mg	−11.89	−0.793	0.3	0.75	1.191
	Cr	12.59	0.839	0.1	0.25	0.7042
	Mn	4.196	0.2797	0	0	0.0782
	Y	−24.48	−1.632	0.3	0.75	3.226
Fe	Ce	−47.58	−3.172	0.7	1.75	13.124
Ni	Ce	−46.40	−3.093	0.7	1.75	12.629
Cu	Ce	−42.97	−2.865	0.8	2.00	12.208
Zn	Ce	−37.59	−2.506	0.5	1.25	7.843
Mg	Ce	−14.38	−0.9583	0.1	0.25	0.9808
Cr	Ce	−46.40	−3.093	0.5	1.25	11.13
Mn	Ce	−33.58	−2.238	0.4	1.00	6.009

If a third element C is added to the A–B system, the intensity of interaction between the A atom and B atom, W'_{AB} , can be estimated as follows:

$$W'_{AB} = W_{AB} + (W_{BC} - \eta) \quad (2)$$

where η is a constant which indicates the shielding effect of the matrix on the interaction between B and C atoms [16]. The concentrations of the TM and Ce in the above-mentioned Al-based amorphous alloys are approximately the same; thus the intensity of the interaction between atoms in the Al–TM–Ce system is expressed as

$$W_{\text{total}} = (W'_{\text{Al-TM}} + W'_{\text{Al-Ce}})/2 = (W_{\text{Al-TM}} + W_{\text{Al-Ce}})/2 + (W_{\text{TM-Ce}} - \eta). \quad (3)$$

In order to study the interaction between atoms, the η -value should first be defined. The relation of the relative solubility changes of elements upon adding 1.0 at.% Ce into Al alloys [16] to $W_{\text{TM-Ce}}$ is shown in figure 6. The solid line represents a simple linear fit:

$$\Delta S = -1.109(W_{\text{TM-Ce}} - 7.837) \quad (4)$$

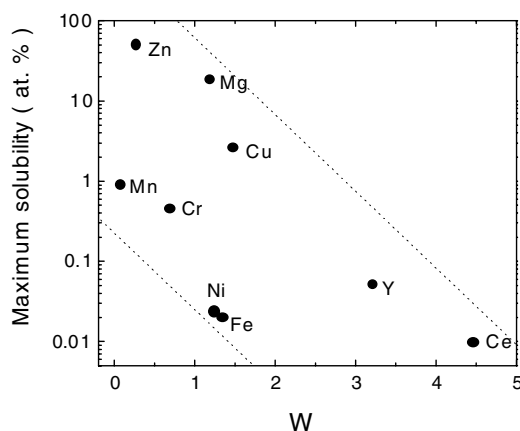


Figure 5. The relation of the maximum solubility of elements in Al alloys and W .

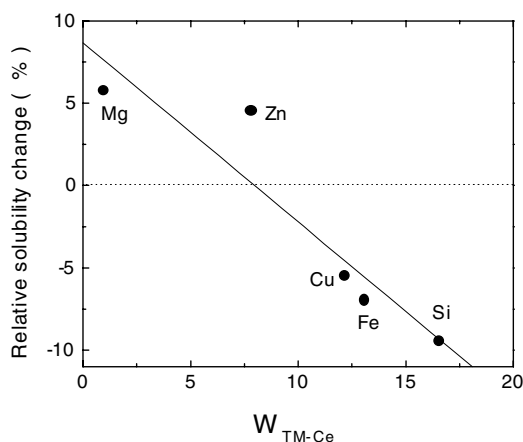


Figure 6. The relation of relative solubility changes of elements in Al alloys and W_{TM-Ce} .

where ΔS is the relative solubility change of the element in the Al alloy. The relative solubility change ΔS would be directly proportional to W_{TM-Ce} without the shielding effect of the matrix on the interaction between TM and Ce atoms. Here, the value of 7.837 represents the shielding effect, so we can consider the η -value to be about 7.837. When $W_{TM-Ce} > \eta$, the interaction between TM and Ce will promote compound formation; otherwise, it will hinder compound formation. Table 3 shows the intensity of the interaction between elements in Al-TM-Ce alloys. From the values of W_{total} , we see that upon adding Ce into the Al-Mg alloy the solubility of Mg increases and the compound-forming tendency decreases. However, upon adding Ce into other Al-TM alloys the compound-forming tendency increases. In fact, it has been proved by experimental results [16] that the solubility of Cu in Al-Cu alloys decreases upon adding Ce and the solubility of Mg in Al-Mg alloys increases upon adding Ce. This also indicates that the interaction between atoms, W , can represent the compound-forming tendency.

According to increasing W_{total} , we can arrange the TM elements in the following order: Mg, Mn, Zn, Cr, Cu, Ni, Fe. This order is nearly identical to the order determined on the basis of the standard free energy of formation of equilibrium products in the Al-TM-Ce system or the standard free energy of formation of their oxides [17]. The strong interaction between

Table 3. The intensity of the interaction between elements in Al–TM–Ce alloys.

Alloy	$W_{\text{Al-TM}}$	$W_{\text{TM-Ce}}$	η	W_{total}
Al–Fe–Ce	1.347	13.124	7.837	8.200
Al–Ni–Ce	1.267	12.629	7.837	7.665
Al–Cu–Ce	1.489	12.208	7.837	7.355
Al–Zn–Ce	0.2798	7.843	7.837	2.385
Al–Mg–Ce	1.191	0.9808	7.837	−4.022
Al–Cr–Ce	0.7042	11.130	7.837	5.884
Al–Mn–Ce	0.0782	6.009	7.837	0.4502

atoms can cause strong chemical bonding and have a certain covalent characteristic that is favourable as regards resolving difficulties of atomic rearrangement and crystallization. In another respect, the strong interaction between atoms can improve the stability of metallic glasses and favour Al-based-glass formation. The glass formability of Al–TM–Ce alloys also increases in the above TM order. The amorphous structure can be obtained under the same quenching conditions from $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ but not $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$, which shows that the glass formability of the Al–Zn–Ce alloy is lower than those of Al–Fe–Ce, Al–Ni–Ce and Al–Cu–Ce alloys. Unless one increases the concentrations of Zn and Ce, the Al–Zn–Ce amorphous structure cannot be obtained. The fact that Al–Fe–Ce alloy has the biggest W_{total} -value among these alloys indicates the existence of a much stronger chemical bond, which may cause the CSRO corresponding to the prepeak and the concentration fluctuation as shown in figure 4. Because the W_{total} -value of the Al–Zn–Ce alloy is lower, it still shows certain characteristics of phase separation or concentration fluctuation. It is thus clear that the experimental results agree with the order of the intensity of the interaction between atoms, W_{total} . From DSC experiments, it is found that the crystallization temperature and crystallization activation energy of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys decrease gradually. This is because of the difference in degree of difficulty of achieving crystallization caused by the interaction between atoms.

The intensity of the interaction between atoms not only reflects the effects of Ce and the TM on Al-based-glass formation, but also is a good criterion for determining the stability, formability and compound-forming tendency of Al-based metallic glasses. Therefore, new high-strength low-density metallic materials can be designed by controlling the interaction between atoms and the compound-forming tendency.

5. Conclusions

From XRD and DSC experiments, it is found that the prepeak positions of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys are shifted to smaller angles gradually. The Al–Zn–Ce amorphous alloy was first obtained by adding Ce to improve the compound-forming tendency and prevent phase separation. The difficulty of achieving crystallization of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$, $\text{Al}_{90}\text{Cu}_5\text{Ce}_5$ and $\text{Al}_{83}\text{Zn}_{10}\text{Ce}_7$ amorphous alloys decreases gradually. The intensity of the interaction between atoms, W , can qualitatively reflect the compound-forming tendency and the glass formability. According to increasing order of W -value, we can arrange the TM elements in the following order: Mg, Mn, Zn, Cr, Cu, Ni, Fe. The glass formability and the compound-forming tendency of Al–TM–Ce alloys increase in this order.

Acknowledgment

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