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LETTER TO THE EDITOR

Non-equilibrium solid phases formed by ion mixing in the Zr-Nb system with positive heat of formation

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Abstract. Amorphization was achieved by ion mixing of multilayered films in the Zr-Nb system that has a positive heat of formation (+6 kJ mol⁻¹). Also, two metastable crystalline (MX) phases, both of FCC structure, were formed, at the Nb-rich and Zr-rich ends.

In the last decade, ion beam mixing has been employed to produce numerous non-equilibrium solid phases with either an amorphous or a crystalline structure [1, 2]. To date, some 70 systems have been studied by ion mixing [3], and based on the extensive experimental data obtained from these systems, several empirical models were proposed to predict the glass-forming ability (GFA) of the binary systems from the static properties of the components and the features of the equilibrium phase diagrams [4-7]. Among them, one empirical model proposed by Liu [3] considered the crystal structure of the components and heat of formation of the system (ΔH_f), calculated on the basis of Miedema's theory [8], as the criteria to predict GFA. In recent years, more attention has been paid to systems with a positive heat of formation because the experimental data available from these systems have not been consistent. Moreover, a better understanding of the experimental observations needs to be developed.

In this study, the Zr-Nb system was investigated by ion mixing. The components of the system have different structures: HCP for pure zirconium (BCC when the temperature is higher than about 870 °C), BCC for pure niobium, and no intermetallic compound exists in the equilibrium phase diagram. The ΔH_f of the system is +6 kJ mol⁻¹ at an equiatomic composition.

Zr-Nb multilayered samples were prepared by depositing alternately pure zirconium (99.9%) and pure niobium (99.9%) onto NaCl single-crystal substrates in an electron gun evaporation system with a vacuum level of the order of 10⁻⁵ Pa. The total thickness of the films was about 50 nm which approximately corresponds to the projected range plus projected range straggling of the irradiation ions, i.e. 200 keV xenon ions. The number of layers for each sample was 6-7 and the thickness of each layer varied from about 4.0 nm to 13.0 nm for zirconium and from about 12.0 nm to 2.0 nm for niobium, respectively, accompanying the component changes of the films. As-deposited films were then irradiated at room temperature with 200 keV xenon ions to doses from 3×10^{14} to 1×10^{16} Xe⁺ cm⁻². The vacuum level during irradiation was better than 5×10^{-4} Pa and the current density was less than 1 μ A cm⁻² in order to avoid overheating. Multilayered

samples of four stoichiometries were selected to carry out transmission electron microscopy (TEM) observations and selected area diffraction (SAD) to identify the resultant phases. In particular, all the average compositions of the final observed phases by ion mixing were confirmed to be unchanged, through energy dispersive spectrum (EDS) analysis within an experimental error of 5%.

The phase evolution of the Zr–Nb multilayered films upon room-temperature 200 keV xenon-ion mixing is listed in table 1. From this table, one can see that among the four selected stoichiometries, two samples with atomic concentrations of $Zr_{40}Nb_{60}$ and $Zr_{88}Nb_{12}$ were amorphized at a dose of $1 \times 10^{16} \text{ Xe}^+ \text{ cm}^{-2}$, as shown in figure 1, while the other two, $Zr_{19}Nb_{81}$ and $Zr_{68}Nb_{32}$, were not amorphized. These results suggest that the composition range favouring amorphization in the Zr–Nb system lies in two discontinuous composition regimes in the equilibrium phase diagram.

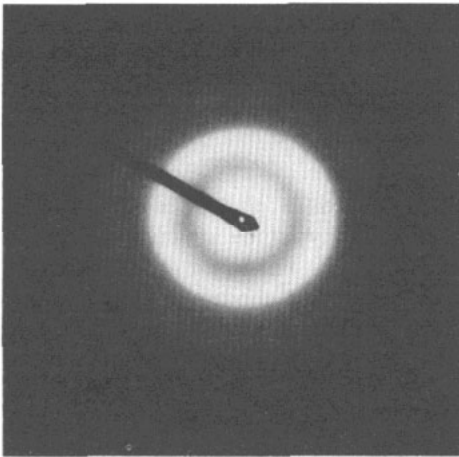


Figure 1. Selected area diffraction pattern of the $Zr_{40}Nb_{60}$ amorphous phase formed by room temperature 200 keV xenon ion mixing of Zr–Nb multilayered sample to a dose of $1 \times 10^{16} \text{ Xe}^+ \text{ cm}^{-2}$.

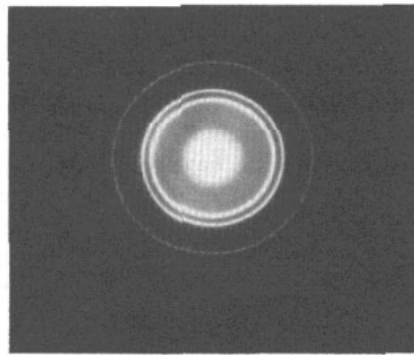


Figure 2. Selected area diffraction pattern of Nb-rich FCC phase formed in $Zr_{19}Nb_{81}$ multilayered sample by room temperature 200 keV xenon ion mixing to a dose of $7 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$. A similar diffraction pattern of Zr-rich FCC phase was also obtained in $Zr_{88}Nb_{12}$ multilayered sample to a dose of $3 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$.

Two new MX phases were formed in the $Zr_{19}Nb_{81}$ and $Zr_{88}Nb_{12}$ films at the irradiation doses of 7×10^{14} and $3 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$, respectively, as also shown in the table. Both the MX phases have FCC structures with different lattice parameters determined to be 4.35 Å for the Nb-rich phase (shown in figure 2 and table 2) and 4.80 Å for the Zr-rich phase. Interestingly, in the $Zr_{68}Nb_{32}$ film, two FCC phases were formed simultaneously and coexisted at a dose of $7 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$, with the lattice parameters determined to be 4.40 Å and 4.73 Å, respectively (see table 3). These two FCC phases can be considered the same as those formed in $Zr_{19}Nb_{81}$ and $Zr_{88}Nb_{12}$ films, respectively, because of the closeness of the measured lattice parameters. Upon further irradiation to a dose of $5 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$, they transformed into a unique FCC phase, with a lattice parameter of 4.35 Å which was the same as the Nb-rich FCC phase observed in the $Zr_{19}Nb_{81}$ sample. It is supposed that another phase should exist in the $Zr_{68}Nb_{32}$ sample at this dose, but only one weak diffraction line was observed and could not be identified.

Table 1. Phase evolution induced by 200 keV xenon ion mixing in Zr-Nb multilayered films.

Sample	Structure obtained after various doses irradiation ($\text{Xe}^+ \text{cm}^{-2}$)		
	7×10^{14}	3×10^{15}	1×10^{16}
$\text{Zr}_{19}\text{Nb}_{81}$	FCC $a = 4.35 \text{ \AA}^a$	The same phase as obtained at former dose	
	7×10^{14}	3×10^{15}	1×10^{16}
$\text{Zr}_{40}\text{Nb}_{60}$	—	—	Amorphous
	7×10^{14}	5×10^{15}	1×10^{16}
$\text{Zr}_{68}\text{Nb}_{32}$	FCC(1) + FCC(2) ^b	FCC $a = 4.35 \text{ \AA}$	The same phase as obtained at 5×10^{15}
	7×10^{14}	3×10^{15}	1×10^{16}
$\text{Zr}_{88}\text{Nb}_{12}$	—	FCC $a = 4.80 \text{ \AA}$	Amorphous

^a a refers to the lattice parameter of the MX phases.

^b FCC(1) and FCC(2) refer to the different MX phases with lattice parameters 4.40 Å and 4.73 Å, respectively.

Table 2. Identification of the formed FCC structure in $\text{Zr}_{19}\text{Nb}_{81}$ multilayered films by 200 keV xenon ion mixing at a dose of $7 \times 10^{14} \text{ Xe}^+ \text{cm}^{-2}$. Lattice parameter $a = 4.35 \text{ \AA}$.

d_{exp}	Intensity	hkl	d_{cal}
2.51	Strong	111	2.51
2.19	Strong	200	2.17
1.53	Strong	220	1.54
1.31	Medium	311	1.31
1.25	Weak	222	1.25
1.08	Weak	400	1.09
1.00	Weak	331	1.00
0.97	Medium	420	0.97
0.89	Weak	422	0.89
0.84	Weak	333, 511	0.84
0.76	Weak	440	0.77
0.72	Weak	442	0.72

Table 3. Identification of the formed two FCC structures in $\text{Zr}_{68}\text{Nb}_{32}$ multilayered films by 200 keV xenon ion mixing at a dose of $7 \times 10^{14} \text{ Xe}^+ \text{cm}^{-1}$. Lattice parameter $a = 4.40 \text{ \AA}$, except * where $a = 4.73 \text{ \AA}$.

d_{exp}	Intensity	hkl	d_{cal}
2.71	Medium	111*	2.73
2.53	Strong	111	2.54
2.38	Weak	220*	2.36
2.20	Strong	200	2.20
1.67	Weak	220*	1.67
1.56	Strong	220	1.55
1.42	Weak	311*	1.42
1.33	Medium	311	1.33
1.28	Weak	222	1.27
1.08	Weak	400	1.10
0.98	Weak	420	0.98
0.91	Weak	422	0.90

The amorphous phase obtained in $Zr_{88}Nb_{12}$ was not stable. It transformed into an MX (FCC) phase when the sample was re-examined after about one and a half months room temperature ageing. The lattice parameter of the MX phase was 4.91 Å, which is a little bigger than that of the FCC phase obtained at an irradiation dose of $3 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$ in the same film. It is attributed to the recovery of defects induced by ion irradiation.

In order to make clear whether or not the irradiation would significantly change the average composition of the formed phases from the nominal value of the as-deposited films, all the samples irradiated up to a dose of $1 \times 10^{16} \text{ Xe}^+ \text{ cm}^{-2}$ were checked by EDS. Analysis results confirmed that the average compositions of the films did not change, within the experimental error.

As for the MX phase of FCC structure emerging at the Nb-rich side, a similar phenomenon has also been observed in the Co-Nb system, in which an intermediate phase of HCP structure was found, suggesting a two-step phase transition of BCC-HCP-FCC [9]. It is well known that it is a little difficult to transform BCC into FCC structure directly, but it is easier to transform first to an HCP and then to an FCC structure. The mechanism of the phase evolution observed in this study and the calculation of the energetic states of those phases are worthy of further discussion, and this project is being undertaken by this group.

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