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LETTER TO THE EDITOR

## Correlation of electron/atom ratio with structural stability in Mo–Fe, Mo–Co and Mo–Ni alloys

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**Abstract.** A BCC→HCP→FCC, structural change was observed in the  $\text{Mo}_{1-x}\text{M}_x$  ( $M = \text{Fe, Co, Ni}$ ) multilayered films irradiated by 200 keV xenon ions at room temperature when  $x$  was less than 30 at %. The structural change in the  $\text{Mo}_{1-x}\text{M}_x$  alloy films was correlated to the electron/atom ratio change due to a d→d electron transfer between Mo and M while alloying. The critical composition for this change was predicted for the three systems using the energy differences among the BCC, HCP and FCC structures of the transition metals calculated from the electronic band theory. The calculated compositions agreed reasonably well with the experimental results.

The crystal structure sequence at ambient pressure for the d transition elements has been accurately accounted for by means of *ab initio* local-density calculations [1] almost a decade ago. From the electronic band structure calculations [2, 3], two rather similar relationships, i.e. the energy difference between BCC and FCC and that between HCP and FCC structures are obtained as a function of the electron/atom ratio and are shown in figure 1. It shows that with increasing electron/atom ratio, the most stable structures are HCP→BCC→HCP→FCC for the transition metals. For the refractory metals with either 5 or 6 valence electrons/atom, BCC is the most stable structure at ambient pressure. Structural transitions, however, like BCC→HCP [4], BCC→FCC [5, 6] and BCC→HCP→FCC [7] have been observed in the BCC refractory metals under ultrahigh pressure [8–10]. These structural transitions are believed to be due to an increase of the d-electrons/atom ratio caused by a pressure-induced sp→d electron transfer under ultrahigh pressure [4, 6]. Similarly, when two transition metals form an alloy, a common d band is always formed through a d→d transfer to minimize the total energy of the alloy [11]. Nevertheless, when the refractory metals alloy with the 3d ferromagnetic metals, i.e. Fe, Co and Ni, the d→d transfer between them will result in an increase of the d-electron/atom ratio compared with the pure refractory metals, implying the possibility of the BCC→HCP (or FCC) transition. These structural transitions, i.e. BCC→FCC [12] and BCC→HCP→FCC [13–15], have been observed in some refractory metals of 5 valence electrons such as Nb and Ta alloying with Fe, Co and Ni of more d electrons. It is of much interest to investigate the possibility and give insight into the same transitions in other refractory metals of 6 valence electrons (such as Mo) when alloying with 3d ferromagnetic metals.

In this letter, we present the BCC→HCP→FCC change in  $\text{Mo}_{1-x}\text{M}_x$  ( $x < 30$  at.%,  $M = \text{Fe, Co, Ni}$ ) alloys induced by ion irradiation and the dependence of the transition on the alloy composition.

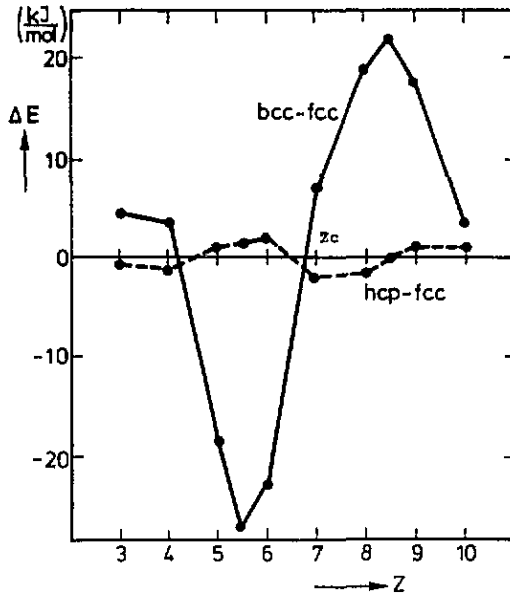


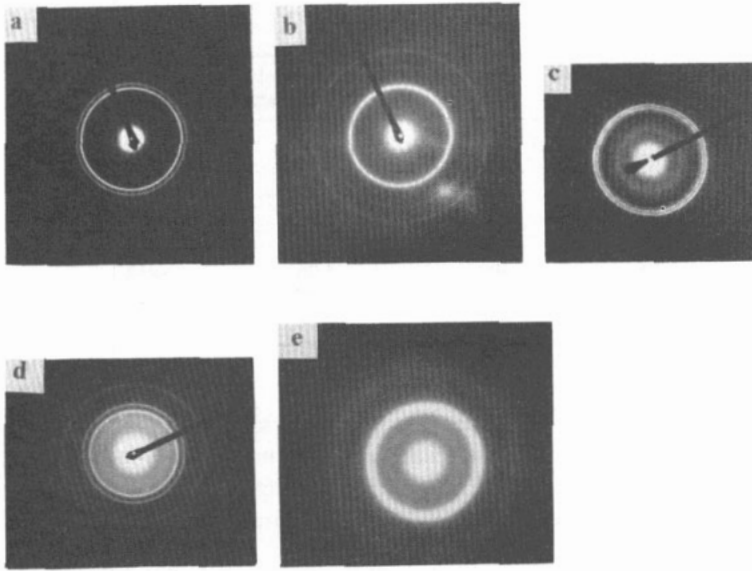
Figure 1. The structural stability energies of the transition metals with the three main crystallographic structures of BCC, HCP and FCC, respectively.

Multilayered  $\text{Mo}_{1-x}\text{M}_x$  films were prepared by alternatively depositing pure molybdenum (99.9%) and pure M (99.9%) onto newly cleaved NaCl single crystals as substrates in an e-gun evaporation system with a vacuum level of the order of  $10^{-7}$  Torr. The as-deposited multilayered films were then irradiated by 200 keV xenon ions at room temperature in an implanter of a vacuum level on the order of  $10^{-6}$  Torr. During irradiation, the beam current density was controlled to be less than  $1 \mu\text{A cm}^{-2}$ , to minimize the beam heating effect. After irradiation, all the irradiated samples were analysed by transmission electron microscopy (TEM) and selected area diffraction (SAD) to identify the structures of the resultant phases. Meanwhile, energy dispersive spectrum (EDS) analysis was employed to determine the real composition of the phase with an experimental error less than 5 at.%.

Table 1. Structural change in the Mo-Fe, Mo-Co, Mo-Ni multilayered films upon room temperature 200 keV xenon ion mixing.

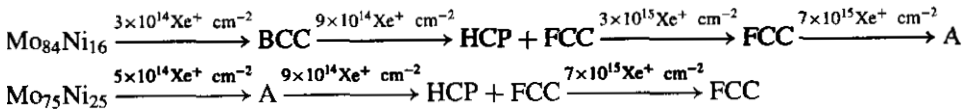
Dose ( $\times 10^{14}$ )	$\text{Mo}_{84}\text{Ni}_{16}$	$\text{Mo}_{75}\text{Ni}_{25}$	$\text{Mo}_{77}\text{Co}_{23}$	$\text{Mo}_{73}\text{Fe}_{27}$
3	BCC	Mo + Ni	Mo + Co	Mo + Fe
5	BCC	A	BCC	BCC
7	BCC	A	HCP + FCC	BCC
9	HCP + FCC	HCP + FCC	HCP + FCC	HCP + FCC
30	FCC	HCP + FCC	HCP + FCC	FCC
50	FCC	HCP + FCC	FCC	FCC
70	A	FCC	A	A

Table 1 lists the structural changes of the  $\text{Mo}_{1-x}\text{M}_x$  alloys with increasing irradiation doses. The structure of the  $\text{Mo}_{84}\text{Ni}_{16}$  multilayered films was BCC when the irradiation dose was  $3 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$ , then it transformed into a mixture of HCP plus FCC structures when the irradiation dose reached  $9 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$ , and when the irradiation dose reached



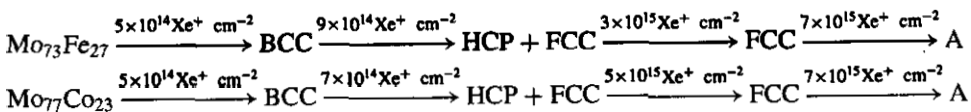
**Figure 2.** SAD patterns of the  $\text{Mo}_{84}\text{Ni}_{16}$  multilayered films at various irradiation stages by 200 keV xenon ion: (a) as-deposited; (b) BCC solid solution; (c) HCP + FCC phases; (d) FCC phase; and (e) amorphous phase.

$3 \times 10^{14} \text{Xe}^+ \text{cm}^{-2}$ , it changed into a uniform FCC structure. The FCC structure was not stable upon further irradiation and turned completely amorphous at a dose of  $7 \times 10^{15} \text{Xe}^+ \text{cm}^{-2}$ . Figure 2(a)–(e) shows the SAD patterns of the  $\text{Mo}_{84}\text{Ni}_{16}$  films at different irradiation stages. The lattice parameters of the HCP and FCC structures are identified to be  $a_{\text{HCP}} = 2.94 \text{ \AA}$ ,  $c_{\text{HCP}} = 4.79 \text{ \AA}$  with a  $c/a$  ratio of approximately 1.63, and  $a_{\text{FCC}} = 4.22 \text{ \AA}$ . Table 2 lists the indexing results of the FCC phase. Interestingly, the same HCP and FCC metastable crystalline phases were also formed in the  $\text{Mo}_{75}\text{Ni}_{25}$  multilayered films under ion irradiation yet in a reverse sequence versus the amorphous phase. It is worthwhile mentioning that the amount of xenon contained in the films was very small. Our EDS analysis revealed that there was less than 3 at.% of xenon in the films at a dose of  $7 \times 10^{15} \text{Xe}^+ \text{cm}^{-2}$ , and thus has negligible effect on the phase formation. The structural change in the  $\text{Mo}_{1-x}\text{Ni}_x$  alloys can be summarized as



Note that A stands for the amorphous phase, BCC is a Mo-rich solid solution, HCP and FCC are the two metastable crystalline phases.

In the  $\text{Mo}_{73}\text{Fe}_{27}$  and  $\text{Mo}_{77}\text{Co}_{23}$  multilayered films, the HCP and FCC phases were also obtained at relative irradiation doses. These results are summarized as follows



Obviously, the HCP and FCC structures in the  $\text{Mo}_{1-x}\text{M}_x$  alloys were formed from the BCC Mo-rich solid solution via a two-step transition of  $\text{BCC} \rightarrow \text{HCP} \rightarrow \text{FCC}$ , where HCP acted

**Table 2.** Identification of the FCC phase formed in the  $\text{Mo}_{84}\text{Ni}_{16}$  multilayered films upon room temperature 200 keV xenon ion mixing to a dose of  $3 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$ .

Planar spacing (experimental)	Indexing results ( <i>hkl</i> )	Planar spacing (calculation)	Intensity
2.44	111	2.44	strong
2.12	200	2.11	strong
1.51	220	1.49	medium
1.27	311	1.27	medium
1.21	222	1.22	weak
1.05	400	1.06	weak
0.97	331	0.97	weak
0.94	420	0.94	weak

as an intermediate state. This transition was quite similar to that observed in the Nb-Fe, Nb-Co and Nb-Ni systems [16]. According to the BCC→HCP→FCC transition mechanism [15], the lattice parameters of the HCP and FCC structures are calculated to be  $a_{\text{HCP}} = 2.73 \text{ \AA}$ ,  $c_{\text{HCP}} = 4.45 \text{ \AA}$  and  $a_{\text{FCC}} = 3.86 \text{ \AA}$ , which agreed reasonably with the experimental values.

The following issue is then why the BCC→HCP→FCC transition occurred in the  $\text{Mo}_{1-x}\text{M}_x$  alloys and why at the above compositions. It is well known that when two transition metals form an alloy, a common d-band will be formed to minimize the total energy of the alloy via a d→d transfer resulting in certainly a different electron/atom ratio of the alloy versus that of the matrix metal [4]. According to Midema [17], the number of electrons transferred per atom A,  $Z_{\text{A in A}_x\text{B}_{1-x}}^{\text{A}}$  in a binary alloy of transition metals A-B can be estimated by

$$Z_{\text{A in A}_x\text{B}_{1-x}}^{\text{A}} = f_{\text{B}}^{\text{A}} \overline{Z}_{\text{A in B}}^{\text{A}} \quad (1)$$

with  $\overline{Z}_{\text{A in B}}^{\text{A}} \simeq 0.5(\Phi_{\text{A}}^* - \Phi_{\text{B}}^*)$ , where  $f_{\text{B}}^{\text{A}}$  is a function related to the atomic concentration and atomic volumes of the constituent metals,  $\Phi_{\text{A}}^*$  and  $\Phi_{\text{B}}^*$  are the work functions of metal A and metal B, respectively. In a  $\text{NiMo}_3$  solid solution for example, nickel atom will carry a negative charge of  $-0.22e$ , indicating that the common d-band of the alloy is formed through a d→d transfer from Ni to Mo. This value is small but very significant as it gives a rise to the electron/atom ratio of the alloy which will probably destabilize the BCC structure of the  $\text{NiMo}_3$  solid solution. The BCC→HCP→FCC transition in the  $\text{Mo}_{1-x}\text{M}_x$  alloys is therefore believed to result from the alloying-induced change in the electron/atom ratio, which, as demonstrated by figure 1, determines the structural stability of pure transition metals. It is reasonable to assume that the structural-dependent energies of transition metal alloys will vary systematically and simply as demonstrated by figure 1, with the average number of valence electrons per atom as long as the two metals form a common band of d-type electron states. One sees that when the average valence electrons of the alloys reaches 6.67 electron/atom ( $Z_{\text{c}}$  point), the energetic curves of the BCC, HCP and FCC structures intersect [17], implying that a structural transition from BCC into HCP or FCC is possible. If we take  $Z_{\text{c}}$  as the critical point for the BCC→HCP→FCC transition and neglect the ferromagnetic contributions from Fe, Co and Ni atoms, the composition for the BCC→HCP (or FCC) structural change in the  $\text{Mo}_{1-x}\text{M}_x$  alloys can be calculated by

$$(1-x)Z_{\text{Mo}} + xZ_{\text{M}} = Z_{\text{c}} \quad (2)$$

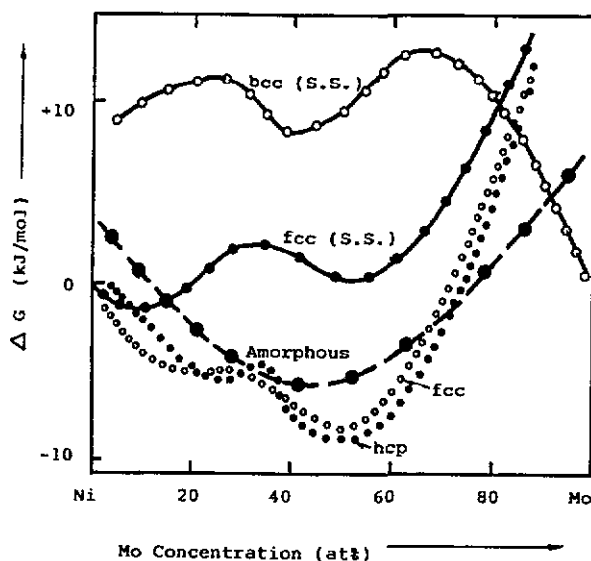


Figure 3. A calculated free energy diagram of the Mo-Ni system

where  $Z_{Mo}$  and  $Z_M$  are valence electrons/atom of Mo and M, respectively. From this equation, the compositions for this transition in the three alloys are calculated to be 33 at.% Fe, 22 at.% Co, and 17 at.% Ni. These values agreed reasonably well with the experimental ones of 27 at.% Fe, 23 at.% Co and 16 at.% Ni.

To elucidate the formation of the amorphous phase in the three systems, the relative energetic levels of the amorphous state and the HCP and FCC structures should be evaluated. Following the well documented literature [18], the free energy diagrams of the three systems, including the free energy curves of the amorphous phase, the two-terminal solid solutions and the HCP and FCC structures were calculated. Figure 3 shows a calculated free energy diagram of the Mo-Ni system. One sees that at the composition around  $Mo_{75}Ni_{25}$ , the amorphous phase is of higher free energy than that of the HCP and FCC structures, while at  $Mo_{84}Ni_{16}$  the free energy of the amorphous phase is lower than that of the HCP and FCC structures. The most possible sequence of phase formation upon ion irradiation is then  $BCC \rightarrow HCP$  (or  $FCC$ )  $\rightarrow A$  at  $Mo_{84}Ni_{16}$  and  $BCC \rightarrow A \rightarrow HCP$  (or  $FCC$ ) at  $Mo_{75}Ni_{25}$ , which is the exact case described above.

In conclusion, a  $BCC \rightarrow HCP \rightarrow FCC$  transition was induced in the  $Mo_{1-x}M_x$  ( $M = Fe, Co, Ni$ ) alloys by room-temperature 200 keV xenon ion irradiation. This structural transition was believed to be correlated to the change of electron/atom ratio due to the alloying-induced  $d \rightarrow d$  transfer from Fe, Co and Ni to Mo.

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## References

- [1] Skriver H L 1985 *Phys. Rev. B* **31** 1909
- [2] Pettifor D G 1977 *Calphad* **1** 305; 1970 *J. Phys. C: Solid State Phys.* **3** 347

- [3] Andersen O K, Madsen J, Poulsen U K, Jepsen O and Kollar J 1977 *Proc. ICM* ed P F de Chatel and J J M Franse (Amsterdam: North-Holland)
- [4] Hixon R S, Boness D A, Shaner J W and Moriarty J A 1989 *Phys. Rev. Lett.* **62** 637
- [5] Singh N 1992 *Phys. Rev. B* **46** 46
- [6] Moriarty J A 1992 *Phys. Rev. B* **45** 2004
- [7] Söderlind P, Ahuja R, Eriksson and Johansson B 1994 *Phys. Rev. B* **49** 9365
- [8] Mattheiss L F and Hamann D R 1986 *Phys. Rev. B* **33** 823
- [9] Jan H J 1984 *Phys. Rev. B* **30** 561
- [10] Chan C T, Vanderbilt D and Louie S G 1986 *Phys. Rev. B* **33** 7941
- [11] Niessen A K and Miedema A R 1983 *Ber. Bunsenges. Phys. Chem.* **87** 717
- [12] Zhang Z J and Liu B X 1994 *J. Phys.: Condens. Matter* **6** 9065
- [13] Zhang Z J and Liu B X 1994 *J. Appl. Phys.* **75** 4948
- [14] Zhang Z J and Liu B X 1994 *J. Phys.: Condens. Matter* **6** 2647
- [15] Liu B X and Zhang Z J 1994 *J. Mater. Res.* **9** 357
- [16] Miedema A R and Niessen A K unpublished
- [17] de Boer FR, Boom R, Miedema W C M, Miedema A R and Niessen A K 1988 *Cohesion in Metals: Transition Metal Alloys* (Amsterdam: North-Holland)
- [18] Liu B X and Zhang Z J 1994 *Phys. Rev. B* **49** 12519