ATOM-PROBE FIELD-ION MICROSCOPY OF MICRO-CLUSTERS IN AN Ni4Mo ALLOY

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ATOM-PROBE FIELD-ION MICROSCOPY OF MICRO-CLUSTERS IN AN Ni_4Mo ALLOY

T. Hashizume, M. Yamamoto* and T. Sakurai

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan
*Department of Materials Science and Engineering, Osaka University, Suita, Osaka 565, Japan

Abstract - Field evaporation of micro-clusters in a Ni_4Mo alloy was studied. When field evaporation was carried out in vacuum, sporadic field evaporation of the surface atoms was frequently observed and the atom-probe analysis resulted in the higher Mo concentration for micro-clusters. We have found that this apparently erroneous composition was caused by simultaneous arrival of more than one ion of the same isotope species at the detector. The appropriate experimental conditions to obtain stoichiometrically correct values of the composition for micro-clusters were then discussed.

I - INTRODUCTION

In alloys, there often exist small regions where the composition differs from the matrix, such as GP-zones and precipitates. Such regions can be called micro-clusters. Since the enviroment of individual atoms in these micro-clusters could be different from those in the matrix, the field evaporation behavior of micro-clusters may well be different in atom-probe field-ion microscope (AP-FIM) analysis /1/. This paper describes problems encounted in the qualitatative atom-probe analysis of micro-clusters and the solutions in the case of a Ni_4Mo alloy.

II - EXPERIMENTAL PROCEDURE

A Ni_4Mo alloy quenched from the high temperature α phase was used as a specimen. The Ni_4Mo alloy in this heating condition is, in the so called, short-range ordered and is considered to be in two phase mixture: the Ni rich α phase and the Mo rich phase containing about 50at%Mo, both of which are very small in size /2,3/. The latter Mo rich phase corresponds to the micro-cluster, in the present case. The crystal structures of both phases are face-centered cubic if ordering is ignored. The method for preparing the Ni_4Mo FIM specimen is described elsewhere /4/.

III - RESULTS AND DISCUSSION

Figure 1 shows the atom-probe data of the field evaporation behavior of the as-quenched Ni_4Mo alloy containing a number of micro-clusters. The experimental conditions during the atom-probe analysis are shown in Table 1. The cumulative number of Ni plus Mo atoms plotted

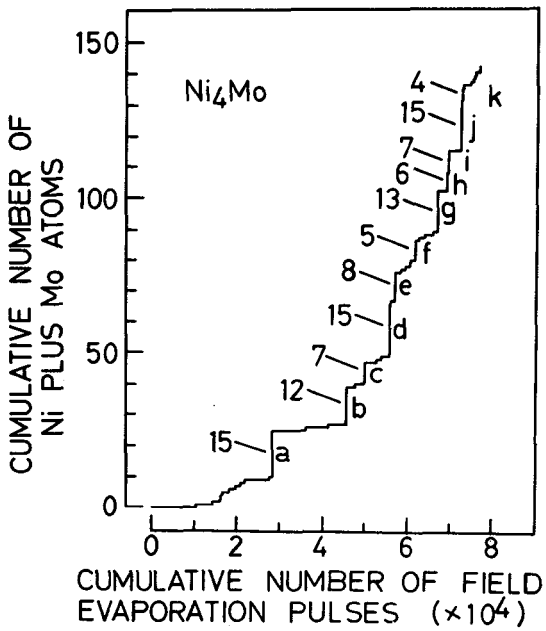

Fig. 1 - Field evaporation behavior of as-quenched Ni_4Mo alloy containing a number of micro-clusters. Experimental conditions during an atom-probe analysis are shown in Table 1.

Table1 Experimental conditions during an atom-probe analysis for Fig.1.

Specimen temperature	20 K
Pulse fraction*	0.1
Background pressure	1.3×10^{-8} Pa
Probed area	high index region near $(111)_{fcc}$

* Pulse fraction is defined by $V_p/(V_{dc}+V_p)$ where V_{dc} is the DC holding voltage and V_p the pulse voltage.

against the cumulative number of evaporation pulses does not increase smoothly, but sporadically on many occasions. The segments of sporadic evaporation are marked by the letters "a" to "k". The total number of signals (Ni and Mo) obtained by the single trigger pulse is also given in the figure. Each of these sporadic field evaporation is caused by one pulse, that is, it is the burst of field evaporation and this field evaporation behavior is due to the existence of micro-clusters in the alloy.

Figure 2(a) shows the number of Mo atoms, and Ni atoms in each cluster in addition to the total number of Ni plus Mo atoms. The total number of atoms in the clusters are in the range of 4 to 15 atoms, except in cluster "a". Note that since a timer with 16 channels has been used to detect signals in this experiment, all the atoms field-evaporated

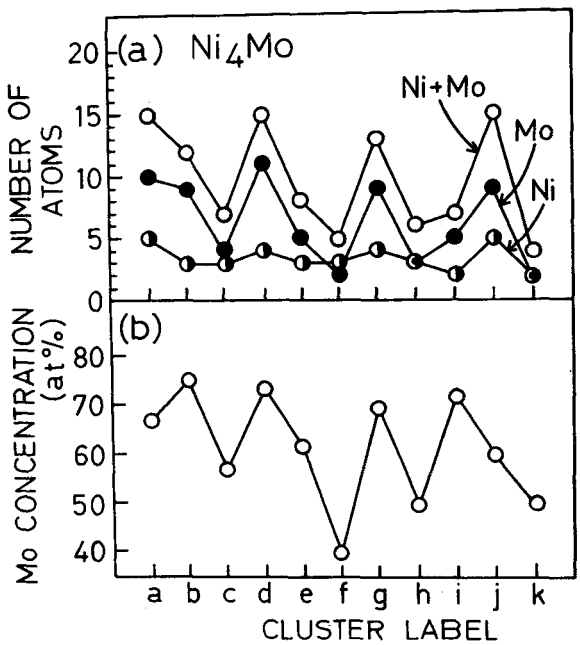

Fig. 2 - (a) Number of Ni, Mo and Ni+Mo atoms of simultaneously field-evaporated clusters a-k. (b) Mo concentrations of simultaneously field-evaporated clusters a-k.

simultaneously by one pulse appear to be successfully detected. For cluster "a", all the channels are filled: one hydrogen atom is simultaneously detected besides ten Ni and five Mo atoms and thus we can not tell whether more atoms reached the detector or not. The number of Ni's is in the range of two to five and mostly three, while that of Mo is two to eleven. The Mo concentrations for the clusters are shown in Fig.2(b). The Mo concentration is in the range of 40 to 76%. These values are significantly higher than the bulk composition (20.1at% Mo). This does not necessarily mean that micro-clusters have the higher Mo concentration. These could be several artifact in the atom-probe compositional analysis. For example, whether a simultaneous field-evaporated segment corresponds to a micro-cluster is not so obvious. Since the number of simultaneously field-evaporated sections is too large in comparison with the volume fraction of micro-clusters in this alloy, 22.6% /3/, we speculate that the sporadic evaporation need not correspond to micro-clusters in the alloy. Some of them may indeed correspond to real micro-clusters in the alloys and others may come from the surrounding matrix after field evaporation of micro-clusters. It is noted that the total number of detected signals and the number of Mo atoms detected fluctuate in the same way (Fig.2(a)). On a basis of those observations, the following mechanism of field evaporation is proposed. First, a micro-cluster field evaporates simultaneously with the surrounding Mo atoms --- a, b, d, g and j in Figs. 1 and 2. Because the micro-cluster, in the present case, is the $L1_0$(M=1)-type ordered phase /3/, bindings among the constituting atoms are strong, and moreover the micro-cluster binds strongly with the surrounding Mo atoms. Note that the binding energy of Mo-Mo is comparable to that of Ni-Mo and is larger than that of Ni-Ni /5/.

The number of atoms evaporated in this sporadic field evaporation is approximately fifteen and is larger than the average number of a micro-cluster, which is ten as described in ref.3. Second, at the detector some of the Ni atoms simultaneously field-evaporated are not counted because of the simultaneous arrival of more than one Ni ion of the same isotope. This will be discussed later. Also, the remaining tip surface is topologically rough, and is Ni-enriched, so that Ni atoms in the protruding surface area field-evaporate by the D.C. holding voltage without the pulse voltage. The apparent surface compositon, thus, becomes rich in Mo. The Mo enriched matrix is still protruded, and then the atoms sporadically field-evaporate. In the case of this evaporation, the size should be smaller than that of a real micro-cluster. c, e, f, h, i and k in Figs. 1 and 2 correspond to this case. The mechanism described above is supported in terms of the number of atoms and the concentration of micro-cluster and also in terms of the volume fraction of micro-clusters in the matrix.

The second artificial effect is the simultaneous arrival of more than two ions of the same species at the detector, as described in the second step of the mechanism. If this occurs, the maximum number and average number can be estimated from statistical consideration in the following way. Table 2 lists the natural abundance and the abundance for Ni_4Mo and NiMo composition, of Ni and Mo isotopes. Ni:Mo=4:1 is the alloy composition, and Ni:Mo=1:1 corresponds to the average composition of micro-clusters in the alloy /3/. On probing the regions with Ni_4Mo or NiMo composition, the maximum number of Ni to be

Table 2 Abundance of Ni and Isotopes

Element	Isotope	Natural Isotopic Abundance	Ni4Mo Phase		NiMo Phase	
Ni	58	68.274	80%	54.6	50%	34.1
	60	26.095		20.9		13.0
	61	1.134		0.9		0.6
	62	3.593		2.9		1.8
	64	0.904		0.7		0.5
Mo	92	15.64	20%	3.2	50%	7.9
	94	9.04		1.8		4.5
	95	15.72		3.1		7.9
	96	16.53		3.3		8.3
	97	9.46		1.9		4.7
	98	23.78		4.8		11.9
	100	9.63		1.9		4.8

detected is five because Ni has five isotopes when a large number of atoms field evaporate at once. However, the Ni isotopes having relatively large natural abundance are only two, ^{58}Ni and ^{60}Ni, and thus the average number of detected Ni is expected to be two, or at most three counting another one from the rest of the Ni isotopes. Indeed, the maximum and average number of detected Ni in Fig.2 are in reasonable accordance with those expected numbers. On the other hand, Mo has not only seven isotopes but also field-evaporates in two kinds of charge states, Mo^{2+} and Mo^{3+}. Thus the maximum number of Mo to be detected is 14. But considering the fact that the number of the Mo atoms in the alloy is not large, the Mo signal level at these clusters might be smaller than 14. Therefore, the number (2-11) of Mo in Fig.2 is reasonable.

The above consideration strongly suggests the simultaneous arrival of ^{58}Ni and ^{60}Ni. In order to examine the simultaneous arrival of two or more ions of the same species at the detector, the signals were monitored by the Tektronix HY-123 storage oscilloscope which allowed us to receive accurate measurements of signal pulse heights. An oscilloscope trace is given in Fig.3. It shows the signals of $^{58}Ni^{2+}$ and $^{60}Ni^{2+}$.

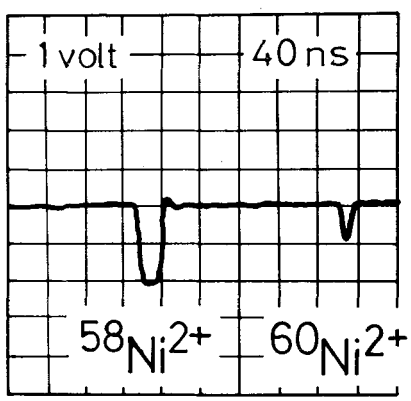

Fig.3 - An oscilloscope trace of $^{58}Ni^{2+}$ and $^{60}Ni^{2+}$, showing simultaneous arrival of four $^{58}Ni^{2+}$.

The peak size of $^{60}Ni^{2+}$ in Fig.3 is found to correspond with a single ion on the basis of repeated detection measurements. The measurement of the areas of $^{58}Ni^{2+}$ and $^{60}Ni^{2+}$ peaks by a microdensitometer shows that the peak of $^{58}Ni^{2+}$ is four times larger than that of $^{60}Ni^{2+}$. This may suggest that four $^{58}Ni^{2+}$ ions were detected simultaneously and registered as a single event in the digital timer.

As a summary, the behavior of the sporadic field evaporation has been interpreted above. Yamamoto and Seidman have discussed nine possible mechanisms or processes which may affect the measured concentration adversely /6/. One of these nine is the simultaneous arrival. We believe that the possibility for the other eight is very low.

Next, to obtain the correct experimental conditions for the probing of micro-clusters in the alloy, various attempts were made. Introduction of He gas of 10^{-5} - 10^{-6} Pa during field evaporation has improved the field evaporation behavior of micro-clusters. Fig.4 shows field-evaporation behavior under He gas of 10^{-5} - 10^{-6} Pa. The experimental conditions used to obtained the results in Fig.4 are the same as those in Table 1 except for the introduction of the He gas. The number of

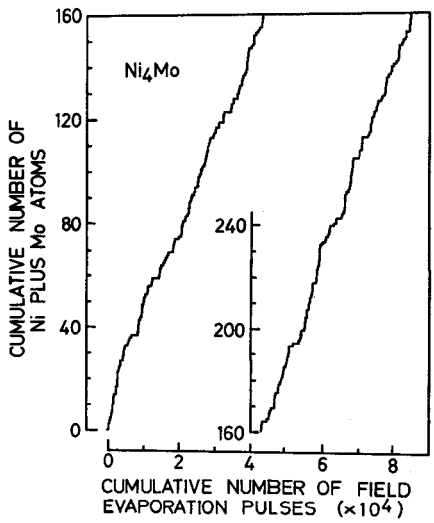

Fig.4- Field-evaporation behavior of as-quenched Ni_4Mo alloy containing a number of micro-clusters, on probing in the presence of He gas of 10^{-5} - 10^{-6} Pa.

field evaporated ions by one voltage pulse is mostly one. In other words, Ni and Mo atoms field evaporates very smoothly. When a probing was made in the presence of H_2 gas, the field evaporation became smooth, but the Mo concentration was found to be higher than expected. It appears that H_2 gas induced selective field evaporation of Ni. In the case of field evaporation in a vacuum, the evaporation field of Mo is higher than that of Ni. Thus, the tightly bound Mo rich micro-clusters persist on the surface. When one of the micro-clusters can not resist to field evaporation, it field evaporates sporadically with the surrounding Mo atoms. On the other hand, in the presence of He gas, He atoms are adsorbed and then the evaporation field of Ni (or Mo) becomes comparable to that of Mo (or Ni). This might result in smooth field evaporation of Ni and Mo in a micro-cluster. As to the pulse fraction, 0.10 was good to obtain stoichiometric composition. When 0.18 was taken as a pulse fraction, the Mo concentration became high although the other experimental conditions remained the same as in the case of Fig.4. Thus, an atom-probe analysis of micro-clusters in Ni_4Mo has been successfully achieved under the appropriate experimental conditions. The details of the microstructure are described elsewhere /3/.

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