ATOM PROBE FIM STUDY OF SHORT RANGE ORDER IN Ni RICH Ni-W AND Ni-Mo-W ALLOYS

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JOURNAL DE PHYSIQUE
Colloque C6, supplément au n°11, Tome 48, novembre 1987

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Abstract - True picture of short range order of Ni rich Ni-W and Ni-Mo-W alloys has been studied by an atom probe FIM. The presence of solute rich regions having about 50at% solute concentration has been found in the Ni-W alloy and in the Ni-Mo-W alloy. The details of these regions are described. Partitioning of Mo and W atoms in the interior and also at the interface, of (Mo+W) rich regions in ternary Ni-Mo-W alloy has been also studied.

I - INTRODUCTION

When Ni rich Ni-W and Ni-Mo-W alloys are quenched from high temperature α phase (fcc) region, their X-ray and electron diffraction patterns show diffuse intensity maxima at 1 1/2 0 and its equivalent positions in addition to the fcc fundamental reflections. Because of the presence of their diffuse intensity maxima, the quenched states of these alloys are called short range ordered. Ni rich Ni-Mo alloys including Ni_4Mo and Ni_3Mo alloys also have similar type of intensity maxima at the same positions of their diffraction patterns in the quenched state and the state is also called short range ordered. The short range order of Ni_4Mo alloy have been studied using an atom probe FIM by Yamamoto et al. /1/, and it was found that there exist a number of fine, Mo rich regions in the matrix of Ni rich solid solution. In the present study Ni rich Ni-W and Ni-Mo-W alloys have been studied to make clear the true picture of the short range order. The results obtained in the present study of both alloys are compared with the results obtained in the previous study of Ni_4Mo alloy /1/.

II - EXPERIMENTAL PROCEDURE

The alloys used have the composition of Ni-16.6at%W and Ni-9.0at%Mo-9.0at%W, which are chemically analyzed values. Hereinafter the two alloys are called Ni-17W and Ni-9Mo-9W alloys, respectively. The value of 16.6at%W is almost the solubility limit of W in Ni solid solution (16.4at%W) /2/. All the specimens were quenched from α phase (fcc) region of 1573 K for a Ni-17W alloy and of 1523 K for a Ni-9Mo-9W alloy. In order to confirm the existence of 1 1/2 0 diffuse intensity maxima, electron microscope observation was made using thin foils of both alloys heat-treated under the same condition as the FIM specimens.

Atom probe FIM analyses were performed employing our atom probe, whose schematic diagram is shown in Fig.1. This atom probe has been slightly improved in the following points from the one described in

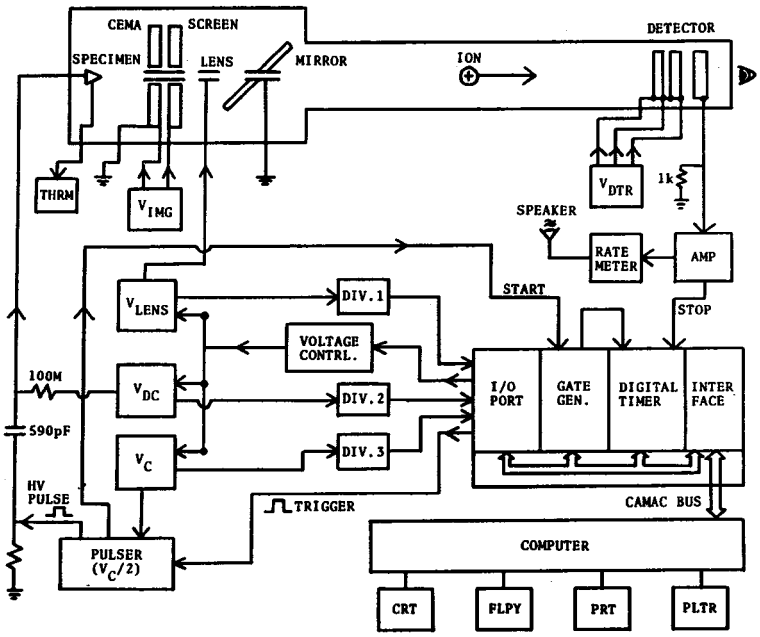

Fig.1 - Schematic diagram of our atom probe FIM.

the previous paper /3/. A pulser is replaced by the pulser with a stack of two mercury-wetted reed relays in order to increase a pulse voltage /4/. To measure time-of-flight of the ions, a digital timer of LeCroy 4208 TDC with eight channels is installed instead of a home made timer and an oscilloscope. All the system are changed to control by an NEC 9801 microcomputer system. As a specimen cooling system, a closed-cycle helium-gas cryogenerator, Cryomini by Osaka Oxygen Industry is used. The cryogenerator also serves as a cryopump.

III - EXPERIMENTAL RESULTS AND DISCUSSION

1. Electron Microscope Studies

The electron diffraction pattern of the quenched specimens of both alloys showed that there were diffuse intensity maxima at 1 1/2 0 and its equivalent positions. Dark field image by the 1 1/2 0 spot did not give any particular contrast.

2. Field-Ion Images

Field-ion images of both quenched alloys showed two characteristics. One is that only low index planes are clearly visible, and the other is that a large number of bright spot cluster appear, randomly dispersed all over the imaging field. These characteristics are, in principle, the same as those in the short range ordered state of Ni_4Mo alloy.

3. Atom-Probe Analyses

Figure 2 is a plot of the cumulative number of W atoms versus the cumulative number of Ni atoms during continuous field evaporation of

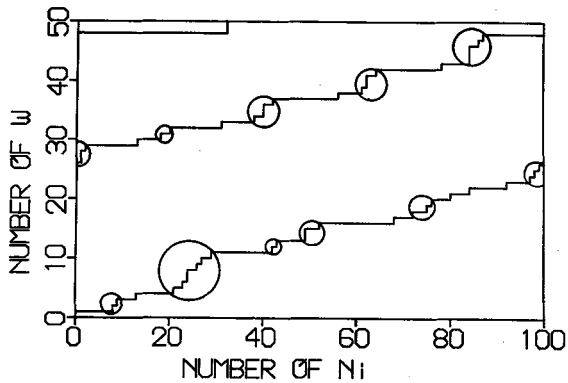

Fig.2 - A plot of the cumulative number of W atoms versus the cumulative number of Ni atoms in a Ni-17W alloy, showing W rich regions indicated by circles.

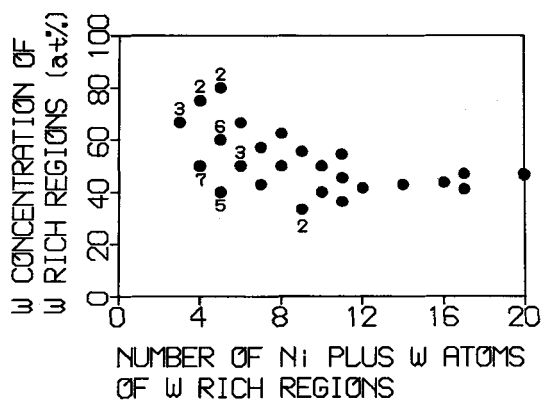

Fig. 3 - A plot of the W concentration versus the number of Ni plus W atoms, in W rich regions of the Ni-17W alloy.

Ni-17W alloy in the atom probe. The slope of this data shows the average composition. The average composition obtained by the present atom probe analysis is 17.8at%W and is in good accordance with the alloy composition (16.6at%W).

However, it is noticed that there exist W rich regions when the data are investigated in detail. If the probed region of the specimen has the stoichiometric Ni_4W composition, four Ni atoms must be detected between W atoms, but there exist a number of regions containing fewer Ni atoms than the Ni_4W composition. The regions containing three or less Ni atoms between W atoms are indicated by the open circles in Fig.2. The W concentration and the number of Ni and W atoms, in those W rich regions, are shown in Fig.3. The numerals in Fig.3 mean the degree of degeneracy at the point. The W rich regions consist of three to twenty atoms and the average value is seven. Compositions of the W rich regions vary in the wide range and its average value is 53.0at%W.

In a ternary Ni-9Mo-9W alloy the same type of analysis was made. The results are shown in Fig.4. Here the discrimination between Mo and W atoms in the rich regions is ignored; the manner of Mo and W within the rich regions is described later. Composition of the (Mo+W) rich regions is widely distributed as shown in Fig.4 and is 53.3 at%(Mo+W) in average.

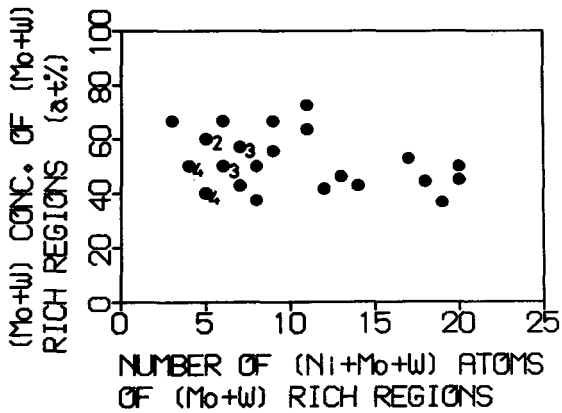

Fig.4 - A plot of the (Mo+W) concentration versus the number of Ni, Mo and W atoms, in (Mo+W) rich regions of the Ni-9Mo-9W alloy.

In Table 1 various parameters characterizing rich regions in both alloys are summarized. In addition, those in Ni_4Mo alloy investigated in the previous work /1/ is also sumarized. When various parameters characterizing rich regions in three alloys are compared each other, the following points are noticed. First, the compositions of the rich regions in all three alloys are far from the alloy composition and are approximately 50at%.

This suggests the presence of the NiX phase where X is Mo, W or (Mo+W). Yamamoto et al., considering together with the appearance of the diffuse 1 1/2 0 spots in both X-ray and electron diffraction, have deduced that $L1_0$(M=1)-type ordered regions and Ni-rich fcc regions, both of which are very small in size, coexist in a quenched state /5/. Note that the $L1_0$(M=1)-type superlattice has the equiatomic

Table 1 Various parameters characterizing rich regions in the three alloys

Name of Alloy	Ni-17W*	Ni-9Mo-9W**	Ni_4Mo+
Composition of Alloy	Ni-16.6at%W	Ni-9.0at%Mo-9.0at%W	Ni-20.1at%Mo
Concentration of Rich Regions	52.5 (at%W)	53.3 (at%(Mo,W))	53.0 (at%Mo)
Number of Atoms	3 - 20	3 - 20	5 - 17
Average	7	9	10
Number of Regions/ 100 Atoms	3.7	3.9	2.3
Volume Fraction (%)	24.5	35.0	23.0

* off-stoichiometric Ni_4W
** off-stoichiometric Ni_4(Mo,W)
\+ the results in ref./1/

composition i.e., it is an AB-type superlattice. Then the above deduction has been confirmed in the previous study of Ni_4Mo alloy /1/. The present atom probe results have shown that the short range order in Ni-17W and Ni-9Mo-9W alloys can also be explained by the above deduction.

However there are some different points between three alloys. In Table 1 the average of the number of atoms in rich region is smaller in Ni-17W alloy than those in the other two alloys. Number of regions per 100 atoms is a value proportional to density and its value is smaller in Ni_4Mo alloy. As to volume fraction, the Ni-9Mo-9W alloy is larger than the others.

The difference between three alloys is considered to be due to the following factors: (i) interaction energy, U_{AA}, U_{BB}, U_{AB}, (ii) composition of alloys, i.e., solute concentration (20.1at%Mo, 16.6at%W and 9.0at%Mo and 9.0at%W), and (iii) quenching temperature.

Interaction energy in Ni-Mo system has been evaluated from the Morse potential energy, cohesive energy, ordering energy ratio and critical temperature for the Ni_4Mo alloy by us /6/. For example, for the first nearest neighbor, the absolute value of U_{AB} is near that of U_{BB}, but is about twice larger than that of U_{AA}. However, so far we have not evaluated interaction energy in the other systems because of lacking of data to be required for calculation.

The difference of solute concentration can be examined by investigation in the same alloy system, say Ni-Mo system. This needs the further work.

The Ni_4Mo alloy was quenched from 1373 K, which is 1.21 T_c and 0.82 T_m where T_c is the critical temperature of order-disorder transformation and T_m is the melting point of an alloy concerned. In Ni_4Mo alloy the peritectoid temperature is used as T_c. The quenching temperature of the Ni-17W alloy is 1573 K which corresponds to 1.27 T_c and 0.87 T_m. The Ni-9Mo-9W alloy was quenched from 1523 K, but the values of T_c and T_m are not known for this alloy. At the moment it seems there is no influence by the difference of the quenching temperature between Ni_4Mo alloy and Ni-17W alloy because of a small difference.

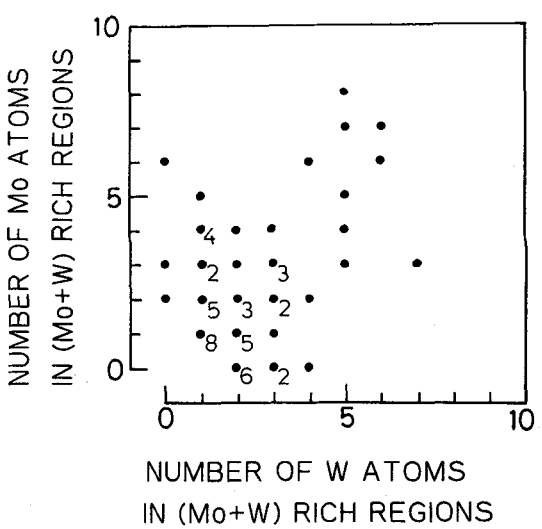

Fig.5 - Partitioning of Mo and W atoms within each of (Mo+W) rich regions of Ni-9Mo-9W alloy

Next, partitioning of Mo and W atoms within each of (Mo+W) rich regions in the Ni-9Mo-9W alloy was analyzed. Figure 5 shows a plot of the number of Mo atoms versus the number of W atoms within (Mo+W) rich regions. The one point corresponds to one region. The numerals in the figure means the degree of degeneracy at the point. If Mo and W atoms play the same role in the rich region, the correlation becomes the positive relation with the slope of unity, that is, both atoms exists the same number each. In Fig.5 the data points distribute in the relatively wide range, but it seems the positive relation with the slope of unity. Thus Mo and W might not have any particular relation.

Atom species at interface between the (Mo+W) rich regions and the matrix have been investigated. Table 2 shows the number of the initial atoms and the last atoms in the rich regions, obtained from atom chain in the atom probe data. If either one of Mo or W atom predominantly segregates to the interface, abundance of the segregated atoms becomes large. However, any combination of the initial and last atoms distributes with roughly the same probability. Thus predominant distribution of either one of Mo and W atoms at the interface is not recognized.

Table 2 Atom species at interface between the (Mo+W) rich regions and the matrix

Event		Number of Events		Abundance (%)	
Initial Atom	Last Atom				
Mo	Mo	18		29.0	
Mo	W	18	29	29.0	46.8
W	Mo	11		17.8	
W	W	15		24.2	
Total		62		100.0	

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