Phase relations in the systems Fe-Ni-Mo, Fe-Co-Mo and Ni-Co-Mo at 1100 degrees C

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PHASE RELATIONS IN THE SYSTEMS Fe-Ni-Mo, Fe-Co-Mo AND Ni-Co-Mo AT 1100 °C

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Summary

We investigated the isothermal cross sections through the ternary phase diagrams Fe-Ni-Mo, Fe-Co-Mo and Ni-Co-Mo at 1100 °C by means of the diffusion couple technique. Essential points of the results were corroborated by an investigation of equilibrated alloys. Use was made of optical, microprobe and X-ray analyses. Characteristics common to the three phase diagrams are the large homogeneity range of the μ phase and the narrowness of the three-phase regions.

1. Introduction

This investigation into the phase relations in the systems Fe-Ni-Mo, Fe-Co-Mo and Ni-Co-Mo fits into the scheme of our work on ternary multiphase diffusion. In a previous paper on the system Ti-Ni-Cu [1] we have already mentioned the fact that only a few isothermal cross sections through multiphase ternary phase diagrams are known at present. In that paper we also pointed out that the diffusion couple technique is an important tool for investigating this type of phase diagrams. Therefore this technique was applied in this investigation together with microprobe and X-ray analyses on selected equilibrated alloys.

In the literature only a few data are given on the ternary systems Fe-Ni-Mo, Fe-Co-Mo and Ni-Co-Mo. In our laboratory the binary systems Fe-Mo, Ni-Mo and Co-Mo have been investigated thoroughly [2 - 4]. Das *et al.* [5] have given information on the 1200 °C isotherms of the three phase diagrams and West [6] has reviewed the Fe-Co-Mo(-Cr) system. These systems are very interesting since the elements involved are the main components of a number of high temperature alloys. Also the diagrams are relatively simple and, therefore, well suited to an investigation of the diffusion paths and the morphology of the diffusion zones and to a comparison with the possible paths indicated by Kirkaldy and Brown [7].

2. Experimental procedure

In this investigation we used molybdenum sheet 1 mm thick (99.9%, Halewood), iron rod (99.95%, MRC), nickel rod (99.99%, MRC) and cobalt strip 0.25 mm thick (99.9%, MRC).

The various binary and ternary alloys were prepared by repeated argon arc melting, after which they were homogenized at 1100 °C for 3 - 10 days in sealed evacuated silica capsules. Diffusion couples were made by solid state resistance welding of the mechanically polished slices of the couple halves in a modified argon arc-melting equipment. A good weld was obtained by clamping the couple constituents between two pieces of carbon rod and then passing an electric current through the assembly. Molybdenum sheets were placed between the carbon rods and the couple to prevent carbon contamination.

During the welding procedure no diffusion layer was formed. The couples were then heated in sealed evacuated silica capsules at 1100 °C for 3 - 10 days. After the heat treatment the alloys or diffusion couples were embedded, ground, polished and etched in a mixture of equal volumes of concentrated HNO₃, H₂SO₄ and H₃PO₄. In order to distinguish the equilibrium α -Fe (b.c.c.) solid solution from the α phase resulting from transformation of the equilibrium γ -Fe (f.c.c.) solid solution during cooling, use was made of CuCl₂ in HCl-ethyl alcohol solution.

The couples and alloys were then investigated using optical microscopy, microprobe analysis and X-ray diffraction. These techniques have been discussed in detail in our previous paper [1].

3. Experimental results

The types of couples used for the investigations of the cross sections through the three phase diagrams at 1100 °C are given in Table 1 together

TABLE 1

Types of couples, together with the phases found at 1100 °C according to microprobe analysis and X-ray diffraction

<i>Fe-Ni-Mo system</i>		<i>Fe-Co-Mo system</i>		<i>Ni-Co-Mo system</i>	
<i>Couple type</i>	<i>Phases</i>	<i>Couple type</i>	<i>Phases</i>	<i>Couple type</i>	<i>Phases</i>
Mo-Fe	Mo- μ - α - γ	Mo-Co	Mo- μ - θ - γ	Mo-Ni	Mo- δ - γ
Mo-Fe ₈₀ Ni ₂₀	Mo- μ - γ	Mo-Fe ₉₀ Co ₁₀	Mo- μ - α - γ	Mo-Ni ₈₀ Co ₂₀	Mo- δ - γ
Mo-Fe ₆₀ Ni ₄₀	Mo- μ - γ	Mo-Fe ₇₀ Co ₃₀	Mo- μ - γ	Mo-Ni ₆₀ Co ₄₀	Mo- μ - γ
Mo-Fe ₄₀ Ni ₆₀	Mo- μ - γ	Mo-Fe ₅₀ Co ₅₀	Mo- μ - γ	Mo-Ni ₄₀ Co ₆₀	Mo- μ - γ
Mo-Fe ₂₀ Ni ₈₀	Mo- δ - γ	Mo-Fe ₁₀ Co ₉₀	Mo- μ - γ	Mo-Ni ₂₀ Co ₈₀	Mo- μ - γ
Fe ₂₀ Ni ₈₀ - μ -(Fe ₇ Mo ₆)	γ - μ	Fe- μ -(Co ₇ Mo ₆)	γ - α - μ	Ni- μ -(Co ₇ Mo ₆)	γ - μ
Ni-Fe ₉₁ Mo ₉	γ - α	Co-Fe ₉₁ Mo ₉	γ - α	Ni ₈₀ Co ₂₀ - μ -(Co ₇ Mo ₆)	γ - μ
				Ni- θ -(Co ₉ Mo ₂)	γ - θ

with the layers developed. All the layers were single phase and were bounded by planar interfaces. The nominal compositions of the most relevant alloys are given in Table 2 together with the equilibrium phases present in the three ternary systems after homogenization at 1100 °C.

The results from phase analyses and equilibrium concentration measurements in diffusion couples and equilibrated alloys led to the cross sections represented in Figs. 1 - 3.

TABLE 2

Phases found in equilibrated alloys at 1100 °C according to microprobe analysis and X-ray diffraction^a

<i>Fe-Ni-Mo system</i>		<i>Fe-Co-Mo system</i>		<i>Ni-Co-Mo system</i>	
<i>Alloy</i>	<i>Phases</i>	<i>Alloy</i>	<i>Phases</i>	<i>Alloy</i>	<i>Phases</i>
Fe ₅₈ Mo ₄₂	μ	Co ₅₅ Mo ₄₅	μ	Ni ₃₀ Co ₁₅ Mo ₅₅	$\text{Mo} + \delta + \mu$
Fe ₂₀ Ni ₃₄ Mo ₄₆	μ	Co ₃₆ Mo ₆₄	$\text{Mo} + \mu$	Ni ₆₁ Co ₈ Mo ₃₁	$\delta + \gamma$
Fe ₄₆ Mo ₅₄	$\text{Mo} + \mu$	Fe ₇₆ Co ₁₁ Mo ₁₃	$\mu + \alpha$	Ni ₄₀ Co ₁₆ Mo ₄₄	$\delta + \mu + \gamma$
Fe ₃₈ Ni ₇ Mo ₅₅	$\text{Mo} + \mu$	Fe ₇₃ Co ₁₄ Mo ₁₃	$\mu + \alpha$	Ni ₃₈ Co ₁₈ Mo ₄₄	$\mu + \gamma$
Fe ₁₉ Ni ₂₅ Mo ₅₆	$\text{Mo} + \mu$	Fe ₇₀ Co ₁₅ Mo ₁₅	$\mu + \alpha + \gamma'$	Ni ₂₂ Co ₅₂ Mo ₂₆	$\mu + \gamma$
Fe ₁₂ Ni ₃₆ Mo ₅₂	$\text{Mo} + \mu + \text{P}$	Fe ₆₄ Co ₂₂ Mo ₁₄	$\mu + \gamma'$	Ni ₁₇ Co ₅₇ Mo ₂₆	$\mu + \theta + \gamma$
Fe ₉ Ni ₂₇ Mo ₆₄	$\text{Mo} + \text{P}$	Fe ₆₀ Co ₂₈ Mo ₁₂	$\mu + \gamma'$	Ni ₁₅ Co ₆₀ Mo ₂₅	$\mu + \theta$
Fe ₂ Ni ₃₈ Mo ₆₀	$\text{Mo} + \delta$	Fe ₄₄ Co ₄₂ Mo ₁₄	$\mu + \gamma'$	Ni ₁₀ Co ₆₈ Mo ₂₂	$\mu + \theta$
Fe ₈₄ Ni ₃ Mo ₁₃	$\mu + \alpha$	Fe ₄₀ Co ₄₈ Mo ₁₂	$\mu + \gamma' + \gamma$	Ni ₅ Co ₇₃ Mo ₂₂	$\mu + \theta$
Fe ₈₂ Ni ₅ Mo ₁₃	$\mu + \alpha + \gamma'$	Fe ₃₇ Co ₄₉ Mo ₁₄	$\mu + \gamma$		
Fe ₈₀ Ni ₇ Mo ₁₃	$\mu + \gamma'$	Fe ₈ Co ₇₁ Mo ₂₁	$\mu + \gamma$		
Fe ₇₄ Ni ₁₁ Mo ₁₅	$\mu + \gamma'$	Fe ₆ Co ₇₃ Mo ₂₁	$\mu + \gamma$		
Fe ₇₂ Ni ₁₄ Mo ₁₄	$\mu + \gamma' + \gamma$	Fe ₃ Co ₇₄ Mo ₂₃	$\mu + \gamma + \theta$		
Fe ₆₈ Ni ₂₀ Mo ₁₂	$\mu + \gamma$				
Fe ₁₅ Ni ₄₇ Mo ₃₈	$\mu + \gamma$				
Fe ₁₂ Ni ₄₄ Mo ₄₄	$\mu + \gamma + \delta$				
Fe ₁₀ Ni ₅₄ Mo ₃₆	$\gamma + \delta$				
Fe ₉ Ni ₅₃ Mo ₃₈	$\gamma + \delta$				

^a γ' indicates that the equilibrium γ phase transforms into α during the cooling procedure.

4. Evaluation of the experimental results

A characteristic common to the three phase diagrams investigated is the large homogeneity region of the μ phase. As expected from the binary phase diagrams, this region covers the full range of $(\text{Fe}_x\text{Co}_{1-x})_7\text{Mo}_6$ compositions. In the Fe-Ni-Mo and Ni-Co-Mo systems, the μ -($\text{Fe}_x\text{Ni}_{1-x}$)₇Mo₆ phase field reaches from $x = 1$ to $x = 0.25$ and the μ -($\text{Co}_x\text{Ni}_{1-x}$)₇Mo₆ field from $x = 1$ to $x = 0.30$.

Another characteristic of these diagrams is the narrowness of the three-phase regions. This obviously stems from the fact that the stability regions of the respective phases δ and μ , $\theta + \gamma$ and $\alpha + \gamma$ nearly touch each other. With regard to the α -to- γ phase transition in iron it can be seen that more cobalt

Fig. 1. The 1100 °C isotherm of the Fe–Ni–Mo system together with some diffusion paths. (Composition scales given in mole fractions.)

Fig. 2. The 1100 °C isotherm of the Fe–Co–Mo system together with some diffusion paths (x, boundary concentrations given by West [6]). (Composition scales given in mole fractions.)

Fig. 3. The 1100 °C isotherm of the Ni–Co–Mo system together with some diffusion paths. (Composition scales given in mole fractions.)

than nickel can be dissolved in an α -Fe solid solution. In the θ -(Co_9Mo_2) phase, much more nickel can be dissolved than iron. As can be seen from Fig. 1, a so-called P phase occurs in the Fe–Ni–Mo system at about the composition $\text{Fe}_{11}\text{Ni}_{36}\text{Mo}_{53}$. This phase has also been found by Das *et al.* [5] in their 1200 °C isotherm but, contrary to our results, they claim the P phase to be in equilibrium with the f.c.c. Fe–Ni–(Mo) solid solution, thus preventing the μ phase coexisting with the δ phase. However, our analysis of the $\text{Fe}_{12}\text{Ni}_{44}\text{Mo}_{44}$ alloy, showing equilibrium between the μ , δ and γ phases, is unambiguous. The X-ray analysis of the P phase in various alloys shows slightly larger orthorhombic lattice parameters than the corresponding P phase in the Cr–Ni–Mo system [8] annealed at 1200 °C (see Table 3).

At the start of our work we did not use molybdenum sheets as a carbon trap during the welding of the couples. In that case we found an additional

TABLE 3

Composition and lattice parameters of the orthorhombic P phase in the Fe-Ni-Mo and Cr-Ni-Mo systems

System	Composition	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
Fe-Ni-Mo	Fe ₁₁ Ni ₃₆ Mo ₅₃	9.091	17.002	4.795
Cr-Ni-Mo [8]	Cr ₁₈ Ni ₄₀ Mo ₄₂	9.070	16.983	4.752

layer which turned out to be the η -carbide phase $\{(\text{Fe}_x\text{Ni}_{1-x})_y\text{Mo}_{1-y}\}_6\text{C}$ with x varying from probably 1 to 0 and y varying from approximately 0.50 at the nickel-rich side to about 0.46 at the iron-rich side. This result is fully in line with former findings of Heijwegen and Rieck concerning the influence of carbon on the interdiffusion of molybdenum and iron [9] and of molybdenum and nickel [10].

With regard to the course of the diffusion paths in the isothermal cross sections we found them to follow the tie-lines in nearly all the couples, *i.e.* only one-phase regions bounded by planar interfaces were involved. Although only this type of couple was used to find the sections given in Figs. 1 - 3, we feel that this restriction is actually unnecessary and needlessly restrictive. This may be illustrated by the one example we found in which a deviating diffusion path occurred, namely in the couple Fe- θ -(Co₉Mo₂). The layer sequence is $\gamma/\gamma + \mu/\theta$ (see Fig. 4). At the boundary where the three phases meet each other we found exactly the same equilibrium concentrations as in the homogenized three-phase alloy Fe₃Co₇₄Mo₂₃. In addition, a large series of tie-lines between the γ and μ phases could be inferred from concentration measurements in the two-phase ($\gamma + \mu$) layer.

Fig. 4. Layer sequence in the diffusion couple Fe- θ -(Co₉Mo₂). The white parts in the diffusion layer are precipitates of the μ phase in a matrix of γ . (Backscattered electron image, Jeol Superprobe 733; magnification, 360 $\times$.)

Also from other systems, such as Cu-Ni-Ti and Fe-Ni-Ti [11], we have evidence that diffusion couples in which polyphase diffusion zones occur, or in which two-phase starting materials are used, are in fact superior for determining the isothermal cross sections through ternary phase diagrams. We have not found any couple in which the measured boundary concentrations deviate from those found in equilibrated alloys, which demonstrates the presence of local thermodynamic equilibrium in all parts of the couple.

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