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Citation for published version (APA):

Laheij, M. A. J. T., Loo, van, F. J. J., & Metselaar, R. (1980). Phase relations in the Fe-Cr-O system at 1200 degrees C investigated by means of a diffusion couple technique. *Oxidation of Metals*, 14(3), 207-215.
<https://doi.org/10.1007/BF00604564>

DOI:

[10.1007/BF00604564](https://doi.org/10.1007/BF00604564)

Document status and date:

Published: 01/01/1980

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Phase Relations in the Fe–Cr–O System at 1200°C Investigated by Means of a Diffusion Couple Technique

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Received January 12, 1979

The morphology and composition of diffusion layers formed in multiphase ternary diffusion couples of Cr or Cr–Fe alloy vs. FeO or FeCr₂O₄ have been studied by electron probe microanalysis, X-ray diffraction, and microscopy. A new technique for annealing of the couples has been developed. Phase relations at 1200°C of the ternary system Fe–Cr–O are discussed, and diffusion paths of the investigated couples are plotted on the isothermal section of the ternary phase diagram.

KEY WORDS: multiphase ternary diffusion; Cr–Fe–O; oxidation of binary alloys.

INTRODUCTION

The phenomenon of oxidation of metals and alloys has been the subject of many investigations. Most of these were based on experimental examination of the oxide layer formed at the surface of the solid phase after reaction diffusion of oxygen gas. For instance, Dalvi and Coates¹ reviewed the applicability of the diffusion path concept to the high-temperature oxidation of binary alloys, starting from alloy–oxygen interface studies.

A different approach was followed by Rapp *et al.*,² who reported work on displacement reactions in metal–metal oxide systems. These authors were interested in the morphologies and reaction rates of the product layers in metal–metal oxide diffusion couples, which were annealed under a

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dynamic flow of argon with a known partial oxygen pressure. From considerations concerning the reaction kinetics they were able to predict the morphologies of the layers formed in the diffusion couple.

Our work is based also on the interaction of a metal or binary alloy with an oxide in multiphase ternary diffusion couples. However, the couples were annealed in a closed system. We believe that this approach is more appropriate to ensure the proper oxygen equilibrium pressure at the interfaces between the various phases.

The purpose of our work was to investigate phase relations in the ternary system iron–chromium–oxygen. To this end, we determined the diffusion paths between FeO and Cr or Cr–Fe alloys and between FeCr_2O_4 and Cr or Cr–Fe alloys. Chromium and iron were chosen for this study because of their important place in the world of construction materials for high-temperature application. Similar experiments on other ternary systems are in progress.

DIFFUSION PATHS IN MULTIPHASE TERNARY SYSTEMS

Kirkaldy and Brown³ developed general rules for the construction of a diffusion path on an isothermal section of the ternary phase diagram. Later these rules were conventionalized by Clark,⁴ as shown in Fig. 1. In Fig. 1a a hypothetical diffusion layer structure of the 100% A vs. 50% B, 50% C

Fig. 1. (a) Hypothetical diffusion layer structure in couple A–BC. (b) The corresponding diffusion path of couple A–BC on the isotherm of the ABC phase diagram. (From Clark.⁴)

couple is illustrated. The lower-case letters relate the region in the diffusion layer structure to the appropriate composition on the ternary isotherm. In Fig. 1b the diffusion path of this hypothetical couple is plotted on the isotherm of the A-B-C phase diagram. All interface structures which are thermodynamically possible in a ternary multiphase diffusion couple are mentioned in this diagram.

For a given couple under conditions of chemical equilibrium the path involves a time-independent sequence of intermediate layers. The plot gives information about the order of the product layers, their morphology, and their compositions; it does not give information concerning the thicknesses of the product layers. The diffusion path approach is a very effective means for the phenomenological description of multiphase ternary diffusion. A better understanding of the course of these paths may lead to the prediction of morphology and composition of oxide scales on binary alloys. We note here that Rapp *et al.*² predicted morphology and composition of product layers by comparing the various diffusion fluxes in the respective layers.

EXPERIMENTAL PROCEDURE

As starting materials we used electrolytic iron and electrolytic chromium. The alloys were prepared in an argon-arc furnace. FeO was prepared according to Brauer⁵ from Fe powder (Merck p.a.) and Fe₂O₃ powder (Merck p.a.). FeCr₂O₄ was prepared according to Whipple and Wold⁶ from (NH₄)₂Cr₂O₇, Fe(NO₃)₃ · 9H₂O, and (NH₄)₂Cr₂O₄ (all Merck p.a.).

The diffusion couple technique applied in this work is illustrated in Fig. 2. The starting materials, a sheet of metal or alloy and the oxide powder,

Fig. 2. Longitudinal section through the reaction vessel.

were compressed in an iron or a stainless steel cylinder by an iron or a stainless steel ram. Under the applied pressure of 5 ton/cm^2 the cylinder and the ram were deformed, which resulted in a fully airtight enclosure of the reactants. The couples were annealed at 1200°C in an evacuated (10^{-2} Torr) quartz glass capsule. After annealing, the couples were quenched to room temperature in water. After this treatment, the cylinders were sawed perpendicular to the sheet surface into two pieces. The dimensions of the cylinder and the annealing time were chosen in order to avoid an overlap of the diffusion layers of the oxide-metal interface with the diffusion layers of the oxide-stainless steel interface. From comparative experiments with a couple of Cr vs. FeO in a stainless steel cylinder and a similar couple in a pure iron cylinder it was concluded that the stainless steel had no influence on the reaction in the couple.

The surface preparation of a couple was very difficult to perform because of the differences in hardness of the successive diffusion layers. The samples were ground on silicon carbide paper and polished with diamond on a nylon cloth.

The diffusion layers between the sintered oxide and the metal or alloy were examined with a Reichert microscope (type MeF2), often using polarized light for additional identification. In some cases the specimens were etched with a solution containing 50 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 20 ml HNO_3 , and 990 ml methanol.

The diffusion layers were analyzed with an electron probe X-ray microanalyzer (A.E.I. SEM IIA). Point measurements were carried out, and both chromium and iron pulses were counted. With these data concentration profiles were calculated using a computer program (Magic 3B, developed by J. W. Colby). By means of X-ray diffraction techniques the various phases in the diffusion zone of the couples were identified. Diffractograms were made using a Philips X-ray diffractometer. Pieces of a diffusion layer were removed and identified by Debye-Scherrer and Guinier powder techniques.

RESULTS

A survey of the diffusion couples investigated is given in Table I. Figure 3 shows the morphology of couple 1. In this couple the starting materials were FeO and Cr. The couple was annealed for 4.5 hr at 1200°C . The photomicrograph shows that the product phases, $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$ and Cr_2O_3 , were formed in a mainly layered arrangement. An exception is the iron formed from the reduction of FeO, which is present in the form of precipitates in the matrix of FeO. This precipitation occurred only in a small region near the interface of $\text{FeO}-\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$.

Table I. Layer Sequence and Morphology of Diffusion Couples After Annealing at 1200°C

No.	Starting materials, at. %	Morphology (mainly)	Layer sequence
1	FeO/Cr	Layered	Cr/Cr ₂ O ₃ /Fe _x Cr _{3-x} O ₄ ^d /FeO + Fe ^b /FeO
2	72Cr, 28Fe/FeO	Layered	Cr-Fe/Cr ₂ O ₃ /Fe _x Cr _{3-x} O ₄ /FeO + Fe ^b /FeO
3	31.3Cr, 68.7Fe/FeO	Layered	Cr-Fe/Cr ₂ O ₃ /Fe _x Cr _{3-x} O ₄ /FeO + Fe ^b /FeO
4	10.7Cr, 89.3Fe/FeO	Internal precipitation	Cr-Fe/alloy + Cr ₂ O ₃ ↓ /alloy + Fe _x Cr _{3-x} O ₄ ↓ /FeO + Fe _x Cr _{3-x} O ₄ ↓ /FeO
5	10.7Cr, 89.3Fe/FeCr ₂ O ₄	Internal precipitation	Cr-Fe/alloy + Cr ₂ O ₃ ↓ /Cr ₂ O ₃ /Cr ₂ O ₃ + alloy ↓ /FeCr ₂ O ₄
6	Cr/FeCr ₂ O ₄	Layered	Cr/Cr ₂ O ₃ /FeCr ₂ O ₄

^a 1 ≤ x ≤ 1.5.^b Isolated precipitates of Fe in a matrix of FeO.

Fig. 3. Photomicrograph of couple FeO vs. Cr (couple 1).

On the isothermal section of the ternary phase diagram of Fe–Cr–O (Fig. 4a) we have constructed the diffusion path corresponding to this couple. As in Fig. 1, the lower-case letters of Fig. 3 relate the region in the diffusion layer structure to the appropriate composition on the ternary isotherm of Fig. 4a. In Fig. 4b an enlarged section is given near the FeO phase field. This clearly indicates the Fe precipitation in the starting material FeO. Similar diffusion paths were observed for samples 2, 3, and 6, which are also plotted on the ternary isotherm of Fig. 4a.

In the diffusion couples 4 and 5 extensive internal precipitation of oxide particles took place. Photomicrograph Fig. 5 shows the reaction layers in sample 4. In the alloy matrix Cr_2O_3 and $\text{Fe}_x\text{Cr}_{3-x}\text{O}_4$ successively precipitated. Figure 5 shows also the transition of the phases γ to α in the Fe–Cr alloy. In Fig. 6 the diffusion paths inferred from couples 4 and 5 are plotted on the isothermal section of the ternary phase diagram.

All determined diffusion paths were reproducible. This means both that within one couple all the paths were the same and that different samples with the same starting materials and treatment showed no deviations from this path.

The couples mentioned in Table I were all infinite in the sense that after annealing the starting materials were still present. From samples, which

Fig. 4. (a) Diffusion paths of couples 1, 2, 3, and 6 on the isothermal section at 1200°C of the ternary phase diagram of Fe-Cr-O (cf. Table I). (b) Enlargement of a section of (a).

were annealed for long periods and accordingly were of the finite type, information was gathered on the isothermal section of the phase diagram. However, these samples could not be used for diffusion path plotting.

DISCUSSION

The experimental diffusion couple technique (couples enclosed in a metal cylinder) has been successfully applied for the investigations of the interaction between solid metals (alloys) and oxides.

Fig. 5. Photomicrograph of couple FeO vs. 10.7 at.%Cr, 89.3 at.% Fe (couple 4).

Fig. 6. Diffusion paths of couples 4 and 5 on the isothermal section at 1200°C of the ternary phase diagram of Fe-Cr-O (cf. Table I).

The diffusion path concept seems to give reliable information about the 1200°C isothermal section of the phase diagram of the investigated system iron–chromium–oxygen.

Our results agree with the phase diagram developed by Pelton and Schmalzried.⁷ However, in this diagram the $\alpha \rightarrow \gamma$ phase transition in the Fe–Cr alloy was not mentioned. The examination of this transition in the alloy phase, e.g., in sample 4, showed that the γ phase is in equilibrium with the Cr_2O_3 phase. This was mentioned before by Whittle *et al.*⁸ Therefore, the α phase of the alloy cannot exist in equilibrium with the spinel phase. This is not in agreement with the isotherms given by Birchenall⁹ and Seybolt.¹⁰

Our results give an extension to the diagram developed by Pelton and Schmalzried.⁷ All samples examined agree with this extended diagram. A rather interesting point in samples 1, 2, and 3 is that all diffusion paths cross the one-phase field of spinel from FeCr_2O_4 to $\text{Fe}_{1.5}\text{Cr}_{1.5}\text{O}_4$. The transition of a layered morphology to a structure with internal precipitation is very interesting and is an important subject for further examination.

REFERENCES

1. A. D. Dalvi and D. E. Coates, *Oxid. Met.* **5**, 113 (1972).
2. R. A. Rapp, A. Ezis, and G. J. Yurek, *Metall. Trans.* **4**, 1283 (1973).
3. J. S. Kirkaldy and L. C. Brown, *Can. Metall. Q.* **3**, 89 (1963).
4. J. B. Clark, *Trans. Metall. Soc. A.I.M.E.* **227** 1250 (1963).
5. G. Brauer, *Handbuch der Preparativen, Anorganischen Chemie* (Ferdinand Euke Verlag, Stuttgart, 1962), p. 1305.
6. E. Whipple and A. Wold, *J. Inorg. Nucl. Chem.* **24**, 23 (1962).
7. A. D. Pelton and H. Schmalzried, *Metall. Trans.* **4**, 1395 (1973).
8. D. P. Whittle, G. C. Wood, D. J. Evans, and D. B. Scully, *Acta Metall.* **15**, 1747 (1967).
9. C. E. Birchenall, in *Oxidation of Metals and Alloys*, D. L. Douglass, ed. (American Society for Metals, Metals Park, Ohio, 1971), pp. 177–200.
10. A. U. Seybolt, *J. Electrochem. Soc.* **107**, 147 (1960).