Alloy oxide equilibria in the Cr-Mn-O system

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Abstract. The phase boundaries of the Cr-Mn-O system have been investigated by alloy-oxide equilibria at 1173 and 1273 K and by isopiestic technique at 1323 K. The oxide phases which coexist in equilibrium with the Cr-Mn alloys are determined by x-ray diffraction studies. The results of the experiments indicate the presence of MnO in equilibrium with Mn-rich alloy whereas $MnCr_2O_4$ and Cr_2O_3 phases coexist with almost pure Cr. A three-phase equilibrium consisting of $MnCr_2O_4$ and MnO phases has been detected at the alloy composition $X_{Mn} = 0.252$ at 1323 K. The composition of the alloy delineates the phase boundaries in the isothermal sections of the system. The results are interpreted by thermodynamic analysis of the Cr-Mn-O system using the data from the isopiestic measurements and those available in the literature.

Keywords. Cr-Mn-O; alloy oxide equilibria; isopiestic technique.

1. Introduction

Chromium and manganese are important components of high temperature alloys. Alloys containing the elements undergo oxidation with the formation of spinel phases during high temperature applications. Information regarding the various types of phases which exist in the Cr-Mn-O system, the stability and proportions of the phases as a function of composition and temperature is important in assessing the applicability of the alloys as high temperature materials. An understanding of the stability of these phases is also important in various thermodynamic studies involving solid state galvanic cells. No studies on thermodynamics and phase equilibria in the system have so far been reported in the literature. Investigations have been carried out to identify various oxide phases and delineate the phase boundaries in the Cr-Mn-O system in equilibrium with Cr-Mn alloys as a function of alloy composition and temperature. The equilibrium phases have been detected by x-ray diffraction studies and the results obtained in the experiments have been interpreted by thermodynamic analysis of the system.

2. Experimental aspects

2.1 *Materials and preparation*

The metals, chromium and manganese were 99·99% pure and supplied by Johnson and Matthey Chemicals, UK and Alfa Products of Thiokal Corporation, USA, respectively. The alloys were prepared by melting weighed quantities of the metals in a recrystallized alumina crucible using a high frequency generator under an atmosphere of pure argon. The gas was purified by passing it over calcium granules heated to 873 K. The alloys were analysed using a Shimadzu spectrophotometer

(UV-visible) after oxidizing a solution containing the alloy to a mixture of permanganate and dichromate as described by Vogel (1969).

Manganese oxide was prepared by reducing Mn_2O_3 in a stream of hydrogen at 1273 K. Manganese chromate was prepared by heating a mixture of potassium manganese chloride, K_2MnCl_4 and lithium chromium oxide, $LiCrO_2$ at 873 K in an atmosphere of pure nitrogen which was dried by passing it over phosphorus pentoxide as described by Busch (1980). Chromium oxide, Cr_2O_3, was prepared by decomposition of chromium carbonate at 1073 K in air. The oxides obtained were then confirmed using an x-ray diffractograph by comparing with d-spacing data available in the literature.

3. Apparatus and procedure

A mixture of an alloy of given composition and a small amount of oxide was repeatedly mixed and ground in an agate mortar to ensure intimate contact between the reactant phases. The alloy-oxide system was heterogenous in nature and fine grinding followed by mixing prior to pelletization was required to enhance the slow solid state diffusion process. The alloy + oxide mixture was pelletized using a steel die to a pellet of about 7 mm dia. The pellet was then enclosed in an outer pellet of MnO as shown in figure 1. Manganese, being a volatile component in the alloys at the temperatures under investigation, the outer pellet of MnO restricts the loss of Mn due to vaporization. The pellet was then introduced in a quartz capsule which was evacuated and filled with argon. It was then re-evacuated and sealed. The quartz capsule was placed carefully in the even temperature zone of a furnace for 720 hr. The furnace zone was controlled within ± 1 K. The time required for the alloy + oxide system to reach equilibrium was determined by several trial runs. At the end of this period, the quartz capsule was quenched in water and the alloy + oxide pellet inside the outer MnO pellet was recovered carefully. An x-ray diffractograph of pellet was then taken after grinding and polishing the surface, to identify the oxide phase present in equilibrium with the alloy at the experimental temperature. Grinding of the alloy + oxide pellet is necessary to avoid any MnO particles adhering to the surface. The equilibrium experiments were carried out at 1173 and 1273 K. Since the alloy phase cannot be separately analysed due to fineness of the grinding and intimate mixing of the reactants, a small quantity of the oxide phase was used to ensure insignificant compositional changes during the experiments. Each alloy composition had been repeated with starting oxide phase as either MnO or $MnCr_2O_4$ separately irrespective of the resultant equilibrium phase as shown in table 1. These repeat experiments were required to ascertain the composition of the alloys in equilibrium with the oxide phases. No side reaction between MnO in the alloy + oxide pellet and quartz was detected by x-ray diffraction studies.
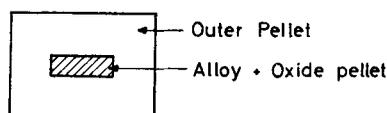

Figure 1. Schematic sketch of an alloy + oxide pellet inserted in a pellet of MnO used in the alloy-oxide equilibrium experiments.

Table 1. Results of the alloy oxide equilibria at 1173 K and 1273 K.

Composition X_{Mn}		0·0		0·264		0·416		0·526	
Starting oxide		$MnCr_2O_4$	MnO	$MnCr_2O_4$	MnO	$MnCr_2O_4$	MnO	$MnCr_2O_4$	MnO
Final oxide	1173 K	—	—	MnO	MnO	MnO	MnO	MnO	MnO
phase at	1273 K	Cr_2O_3 $MnCr_2O_4$	Cr_2O_3 $MnCr_2O_4$	—	MnO	MnO	MnO	—	MnO

	0·579		0·672		0·689		0·735		0·899	
	$MnCr_2O_4$	MnO	$MnCr_2O_4$	MnO	$MnCr_2O_4$	MnO	$MnCr_2O_4$	MnO	$MnCr_2O_4$	MnO
	—	—	MnO	MnO	MnO	MnO	MnO	MnO	MnO	MnO
	—	MnO	—	MnO	MnO	MnO	MnO	MnO	MnO	MnO

4. Isopiestic experiments

A number of alloys were used in the isopiestic experiments in order to establish the compositions of the alloys and the corresponding oxide phases in equilibrium at 1323 K. In these experiments, two alloy pellets of different compositions and an alloy pellet mixed with a small quantity of Cr_2O_3 were taken in the upper part of a quartz capsule as shown in figure 2. The lower part of the capsule contained a pellet of pure Mn. A chromel-alumel thermocouple attached close to it measured the temperature of the pellet. The capsule was then held vertically in a furnace such that the upper part containing the alloy pellets was in the even temperature zone of the furnace. An

Alloy pellets and
alloy + oxide pellet
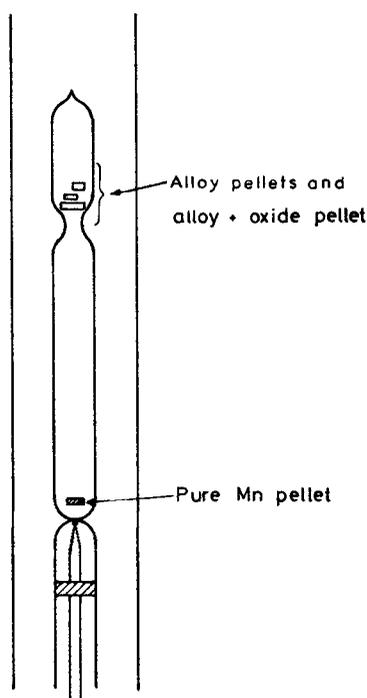
Pure Mn pellet

Figure 2. Schematic sketch depicting the experimental set-up for the isopiestic technique.

additional chromel-alumel thermocouple placed in the zone measured the temperature of the alloy sample. The temperature of the Mn pellet dictated the partial pressure of Mn in the capsule. The system was considered to be in equilibrium as the composition of the alloys placed in the upper part of the capsule approached that of an equilibrium value. The temperature distribution in the furnace was such that the manganese pellet was at a lower temperature than that of the alloy pellets. After the equilibrium which required 500 hr, the capsule was quenched in air. The compositions of the alloy pellets were then determined by chemical analysis using a spectrophotometer as already described. The alloy + oxide pellet was then subjected to x-ray analysis to determine the oxide phase present as shown in table 2. Since two alloy pellets reached the same composition starting from different initial compositions, the composition of the alloy in the alloy + oxide pellet was considered to be the same as that of the other alloy pellets. The initial composition of the alloy in the alloy + oxide pellet was chosen fairly close to those of the other two so that the same equilibrium value could be achieved in the samples. An added advantage of the method is that, apart from the alloy + oxide equilibrium studies, thermodynamics of the Cr-Mn system could also be determined simultaneously. One set of experimental results is reported in table 2. This constitutes a part of a major programme on the determination of thermodynamic properties of Mn-based systems, the details of which are to be published elsewhere.

5. Results and discussion

The tie line compositions of Cr-Mn alloys in equilibrium with the corresponding oxide phases at 1173 and 1273 K are summarized in table 1 and those at 1323 K in table 2. These data indicate that for alloys $X_{Cr} \simeq 1.0$, the stable oxide phases are Cr_2O_3 and $MnCr_2O_4$ irrespective of the starting oxide phase used in the equilibrium experiments. However, as the Mn content of the alloy is increased close to $X_{Mn} = 0.252$, $MnCr_2O_4$ is recognized to be the only oxide phase in equilibrium as determined by the isopiestic technique at 1323 K. The alloy-oxide system exhibits
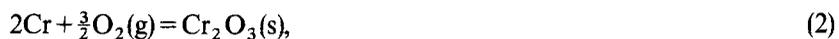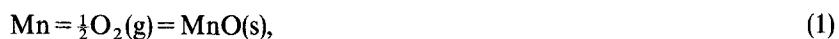
Table 2. Results of isopiestic experiments at temperature 1323 K Starting oxide phase (in all cases): Cr_2O_3.

Composition X_{Mn}	Final oxide phases
0.04	$MnCr_2O_4$
	Cr_2O_3
0.067	$MnCr_2O_4$
0.152	$MnCr_2O_4$
0.188	$MnCr_2O_4$
0.215	$MnCr_2O_4$
0.233	$MnCr_2O_4$
0.252	MnO
	$MnCr_2O_4$
0.337	MnO
0.392	MnO
0.570	MnO
0.586	MnO

similar trends as X_{Mn} tends to 0·252 independent of the starting oxide phase used in the experiments. However, the change-over of the type of oxide phase from $MnCr_2O_4$ to MnO occurs when $X_{Mn} = 0·252$ as shown in tables 1 and 2. The change-over composition is considered to be an important feature which essentially determines the existence of the three-phase equilibrium in the Cr-Mn-O system. Tables 1 and 2 further indicate the existence of a MnO phase in equilibrium with the alloys as X_{Mn} is increased beyond the change-over composition. These compositions roughly demarcate the phase boundaries in the Cr-Mn-O system in terms of the type of oxide phase which coexist in equilibrium with the Cr-Mn alloys as a function of alloy composition and temperature. The results summarized in tables 1 and 2 have been interpreted by thermodynamic calculation in the subsequent section.

6. Thermodynamic analysis

The determination of the isothermal sections of the Cr-Mn-O system is based on equilibrium calculation and information from the constituent binaries. Various alloy phases and their phase boundaries in the Cr-Mn system as a function of composition and temperature were recently computed by Venkataraman and Neuman (1986). These phase designations and boundaries are adopted in the present study. The composition of the alloy in equilibrium with the oxide phases has been determined from thermodynamic properties of the Cr-Mn alloys and equilibrium constants of the following reactions:

$$Mn = \tfrac{1}{2}O_2(g) = MnO(s), \tag{1}$$

$$2Cr + \tfrac{3}{2}O_2(g) = Cr_2O_3(s), \tag{2}$$

$$Mn + 2Cr + 2O_2(g) = MnCr_2O_4. \tag{3}$$

The equilibrium constants of (1), (2) and (3) at 1173, 1273 and 1323 K are obtained from the standard free energy of formation of MnO and $MnCr_2O_4$ respectively. The standard free energy of formation of MnO is obtained from Barin and Knacke (1973) and Barin *et al* (1977) and those of Cr_2O_3 and $MnCr_2O_4$ are available from Chase *et al* (1975) and Jacob (Private Communication) respectively. In order to evaluate the stability of the oxides as a function of alloy composition in the Cr-Mn-O system, thermodynamic properties of the Cr-Mn alloys have been used as reported by Eremenko *et al* (1968) and Jacob (1985) and those from the present isopiestic studies at 1323 K. Thermodynamic properties of the Cr-Mn system have been studied by Eremenko *et al* (1968) at 1023 K using a fused salt emf technique. Their results indicate positive deviations from Raoult's law. In the absence of any enthalpy data or data based on second law evaluation, the activity data as reported by Eremenko *et al* (1968) are used with reference to β Mn as standard state. The calculation assumes the excess free energy property of the Cr-Mn system to be independent of temperature. Figure 3 depicts the variation of $-\log P_{O_2}$ as a function of alloy composition at 1323 K which describes the stability range of various oxides in the Cr-Mn-O system. It also shows that the free energy change of the MnO phase coincides with that of $MnCr_2O_4$ at $X_{Mn} = 0·29$ at this temperature. The calculated values of the change-over composition using the data of Eremenko *et al* (1968) at 1173 and 1273 K are 0·26 and 0·25 respectively. More recently thermodynamic properties of the Cr-Mn
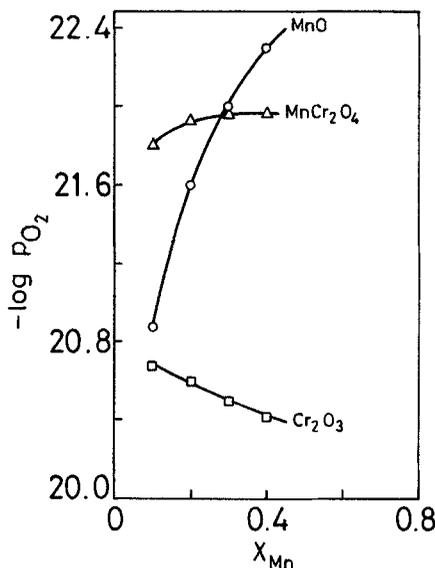
Figure 3. Logarithm of partial pressure of oxygen as a function of composition of the Cr-Mn alloys using the extrapolated data of Eremenko *et al* (1968) at 1323 K.
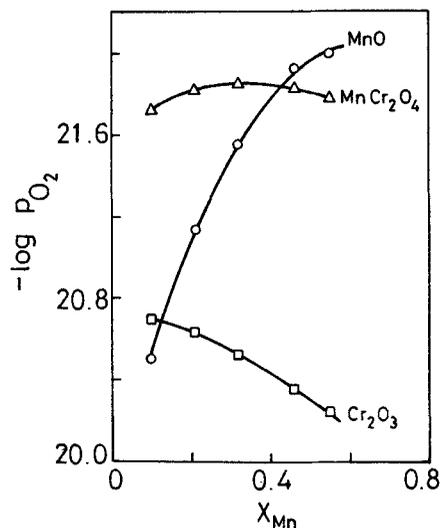

Figure 4. Logarithm of partial pressure of oxygen as a function of alloy composition based on the activity data determined by Jacob (1985) at 1323 *K*.

system for Cr rich b.c.c. solid solution have been measured by Jacob (1985) using Knudsen effusion cell in the temperature range of 1200 to 1500 K. The calculated relationship between the stabilities of the oxide phases and alloy composition at 1323 K based on his data is presented in figure 4. The change-over composition at this temperature may be noted as $X_{Mn} = 0.43$. The corresponding calculated X_{Mn} values at 1173 and 1273 K are 0.41 and 0.38 respectively.

The thermodynamic data of the Cr-Mn system based on the present investigation using isopiestic technique at 1323 K are expressed in terms of the activity coefficients of Mn and Cr, in the range of $0 < X_{Mn} < 0.65$ as

$$\gamma_{Mn} = 2.504 - 1.927 X_{Mn}. \tag{4}$$

and

$$\ln \gamma_{Cr} = 1/0.2305[-0.7695 \ln(1 - X_{Mn}) + \ln(1 - 0.769 X_{Mn})]. \tag{5}$$

Figure 5 depicts the variation of $-\log P_{O_2}$ as a function of alloy composition using (4) and (5) in conjunction with (1), (2) and (3). The calculated change-over composition exists at $X_{Mn} = 0.22$. The latter thermodynamically calculated value is in excellent agreement with $X_{Mn} = 0.252$ which is obtained from alloy-oxide equilibria followed by x-ray diffraction studies as reported in table 2. The change-over composition is considered to be important, as it delineates the phase boundaries of the Cr-Mn-O system. The existence of the three-phase equilibrium at this composition would make the coexistent partial pressure of oxygen imparted by the alloy + MnO to be equal to that by the $MnCr_2O_4$ + alloy phases at 1323 K. Therefore using (1), (3), (4) and (5) at $X_{Mn} = 0.252$, the standard free energy of formation of $MnCr_2O_4$ has been assessed and found to be -1133.86 kJ mole^{-1}. This compares favourably with a value of -1129.68 kJ mole^{-1} as given by Jacob (Private Communication) at 1323 K.

The existence of the other three phase equilibria between Cr, $MnCr_2O_4$ and Cr_2O_3 phases is indicated in tables 1 and 2. Table 3 shows that for an alloy of almost pure Cr, $X_{Mn} = 0.0001$ at 1323 K, the $MnCr_2O_4$ and Cr_2O_3 phases coexist in equilibrium. In this dilute solution range, the activity coefficients of Cr and Mn in the alloy are used based on (4) and (5) such that X_{Mn} tends to unity, γ_{Cr} tends to 1.0 and γ_{Mn} approaches a value of 2.504 at 1323 K. The Cr-rich alloy, however, retains about 4 at % Mn as reported in table 2. This is considered to be due to lack of
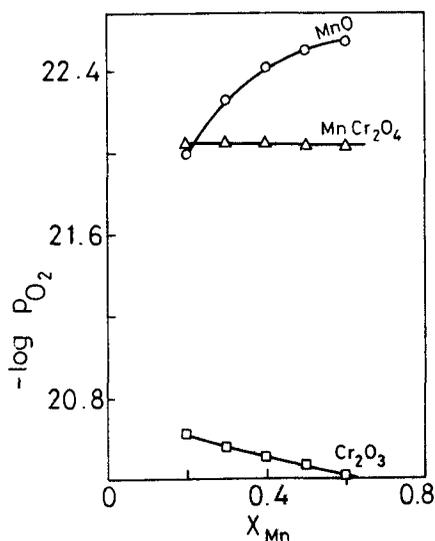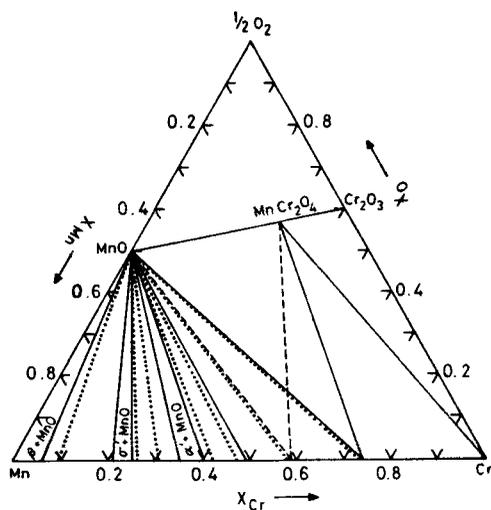

Figure 5. Variation of logarithm of partial pressure of oxygen with the composition of Cr-Mn alloys based on the activity data determined by the isopiestic technique at 1323 K.

Table 3. Three phase equilibrium involving Cr, Cr_2O_3 and $MnCr_2O_4$.

X_{Mn}	$Po_2 MnCr_2O_4$, atm.	Po_2, Cr_2O_3 atm.
0·001	$9·52 \times 10^{-23}$	$1·78 \times 10^{-21}$
0·0001	$3·00 \times 10^{-21}$	$1·78 \times 10^{-21}$

Figure 6. Isothermal section of the Cr–Mn–O system at 1173 K. Comparison between the present data (. . . .) and those calculated based on the activity data of Eremenko *et al* (1968) (———) and Jacob (1985) (———).

thermodynamic equilibrium. It may be mentioned that the starting composition of the alloy was about 6 at % Mn mixed with Cr_2O_3 which is expected to be extremely slow in giving up its Mn content to reach an equilibrium state containing alloy $+ MnCr_2O_4$ phases.

The samples containing either $Cr + MnCr_2O_4$ or $Cr + MnO$, as reported in table 1, reach equilibrium under the experimental conditions used in the alloy-oxide equilibrium studies. Consequently the existence of the equilibrium phases, $MnCr_2O_4$ and Cr_2O_3, has been detected by x-ray analysis of the samples irrespective of their starting oxide phases. The tie line compositions of the Cr-Mn alloys summarized in tables 1 and 2 are shown along with the thermodynamically calculated values in the isothermal sections of the Cr-Mn-O system. Figures 6, 7 and 8 denote the isothermal sections at 1173, 1273 and 1323 K, respectively.

The alloy-oxide equilibria and thermodynamic studies indicate the presence of MnO predominently in the Mn-rich compositions and $MnCr_2O_4$ and Cr_2O_3 in the three-phase equilibrium with almost pure Cr. The change-over of the chromate to MnO phase occurs when $X_{Mn} = 0·252$ at 1323 K which decides the other three phase equilibria in the Cr-Mn-O system.
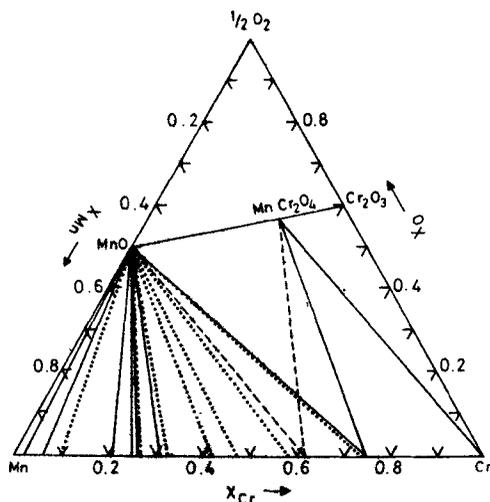
Figure 7. Isothermal section of the Cr-Mn-O system at 1273 K. Comparison between the present data (. . .) and thermodynamically calculated values based on the data of Eremenko *et al* (1968) (————) and Jacob (1985) (———).
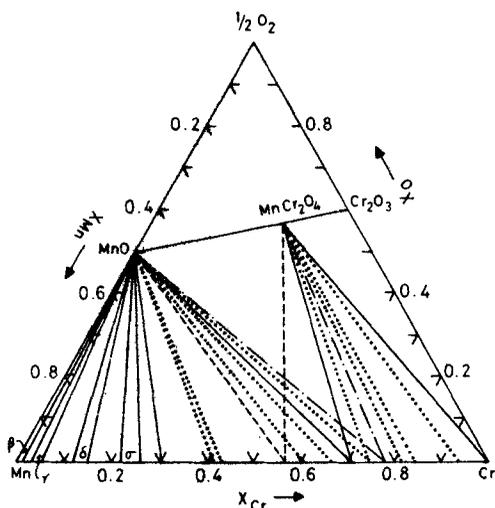

Figure 8. Isothermal section of the Cr-Mn-O system at 1323 K. Comparison between the data of the present work (—·— isopiestic experiment; . . . . ,alloy-oxide equilibrium) with values derived based on Eremenko *et al* (1968) (————) and Jacob (1985) (———).

Acknowledgements

References

Barin I and Knacke O 1973 *Thermochemical properties of inorganic substances* (Berlin: Springer Verlag)
Barin I, Knacke O and Kubaschewski O 1977 *Thermochemical properties of inorganic substances* (Berlin: Springer Verlag) Supplement

Busch D H 1980 *Inorganic synthesis* (New York: John Wiley) Vol. 20

Chase M W, Wrnutt J L, Prophet H and Mcdonald R A 1975 *J. Phys. Chem. Ref. Data* **4** 92

Eremenko V M, Lukashenko G M and Sidorko V R 1968 *Russ. J. Phys. Chem.* **42** 343

Jacob K T 1985 *Z. Metallkde* **76** 415

Venkataraman M and Neuman J P 1986 *Bull. Alloy Phase Diagrams* **7** 457

Vogel A I 1969 *Quantitative inorganic chemistry* (London: ELBS & Longman)