OPTIMUM SLAG–ALLOY RELATIONSHIPS FOR THE PRODUCTION
OF MEDIUM- TO LOW-CARBON FERROMANGANESE

N. A. BARCZA
National Institute for Metallurgy. Randburg. South Africa
and
D. P. O'SHAUGHNESSY
Hatch Associates Ltd. Toronto, Canada

Abstract—Optimum slag–alloy relationships in the production of medium- to low-carbon ferromanganese were studied from data gathered at the Transalloys plant in South Africa and from laboratory-scale tests. A critical basicity ratio was defined for the final slag above which problems would be likely in the separation of the slag from the alloy. The initial melt and alloy compositions and the melt-to-alloy ratios have to be carefully controlled if the alloy produced is to meet the silicon specification and at the same time contain a reasonable proportion of manganese. The recovery of manganese at the required silicon specification in the alloy can be improved by multistage contacting.

Résumé—A partir des données rassemblées à l'usine Transalloys en Afrique du Sud et d'expériences en laboratoire, nous avons étudié les relations optimales scorie-alliages dans la production de ferromanganese de moyen à bas carbone. On a défini, pour la scorie finale, un rapport de basicité critique au delà duquel des problèmes se posent lors e la séséparation de la scorie de l'alliage. Si on veut que l'alliage produit rencontre les spécifications pour le silicium et en même temps contienne une portion raisonnable de manganèse, il faut contrôler soigneusement les compositions du liquide initial et de l'alliage ainsi que les rapports liquide-alliage. La récupération du manganèse au niveau requis en silicium dans l'alliage peut être améliorée par une mise en contact multiétapes.

1. INTRODUCTION

Medium- to low-carbon ferromanganese is produced successfully by two very different techniques. At Union Carbide. as reported by Day [1], high-carbon ferromanganese is decarburized successfully by being blown with oxygen in a converter. Losses of manganese are moderately high, and this, together with the confidential nature of the work, is perhaps the reason for the restricted application of the technique. This approach has been reported by the Russians Geikhman et al. [2] and Romanov et al. [3], and by the Germans Andrejewski et al. [4]. There is also a French–South African patent in which oxygen and steam are used [5].

The method more often used by ferro-alloy producers involves the contacting of a high-grade slag, or a melt of manganese ore and lime that is rich in oxides of manganese, with a silicomanganese reducing agent containing from 16 to 30% silicon. The contacting of the manganese melt and alloy phases can be achieved in an electric smelting furnace (as in Brazil [6]) or in mixing ladles as at Transalloys in South Africa.

The main competitor to medium- to low-carbon ferromanganese is electrolytic manganese. As predicted by Mikolajczak [7] early in 1974, there has been an increased demand for refined ferromanganese alloys since the expansion of the AOD process. but the cost of the extra processing time in the AOD vessel has to be balanced against the cost per unit of manganese. Electrolytic manganese is still used exclusively in the production of very low-carbon high-manganese steels when the carbon content of the refined ferromanganese alloy would be too high. Electrolytic manganese also has a great advantage in its very low phosphorus content (less than 0.001% phosphorus).

The increase in combined manganese content from 1.0 kg to about 1.74 Kg per ton of steel over the past decade can be attributed, according to Mikolajczak [8]. to the development of low-carbon steels (made possible by oxygen-converter processes). The major consumption of low- to medium-carbon ferromanganese takes place in the U.S.A., the U.K., the Federal Republic of Germany, Japan, and the U.S.S.R. [8].

South Africa and the U.S.S.R. have the World's largest reserves of manganese ore. South Africa's reserves are conservatively estimated at about 186 000 million tons [9], and the resources are estimated at some 12 billion tons. The occurrences are mainly in the north-western Cape Province at well-known mines such as Hotazel, Wessels, and Mamatwan. Much of the ore is rich in calcium oxide or carbonate. and is virtually self-fluxing. The ores are therefore ideal for the production of a melt that can be used readily in the processing of low- to medium-carbon ferromanganese. The Pyrometallurgical Research Group* of the National Institute for Metallurgy in South Africa undertook research work in 1973, when it was realized that there was a lack of fundamental knowledge in this field, and the results have been reported by Barcza [10] and Channon [11]. In this research, the rate of reaction between various manganese-containing melts or slags and silicon-containing alloys was determined, and the state of equilibrium attained was measured. This paper summarizes these findings and relates them to plant data, the aim being primarily to discuss the importance of optimum compositions for melt and alloy, and the melt-to alloy ratio necessary for a product that meets the specifications for the silicon. manganese, and carbon contents

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*Based at the University of the Witwatersrand, Johannesburg.

and the physical appearance. (The appearance depends largely on the final slag–alloy separation.) In addition, the use of multistage techniques in the achievement of these objectives is dealt with briefly.

2. LABORATORY-SCALE TESTS

In the experiments, a wider range of compositions of the melt and silicide alloy, and more variable conditions (e.g. melt-to-alloy ratio), were studied than would normally be considered in plant practice. The details of this work are reported elsewhere [10, 11].

2.1 Experimental procedure

According to De Villiers [12], the Mamatwan ore used in many of these tests contains several minerals, mainly braunite, hausmannite, calcite, and dolomite, with minor amounts of bixbyite and hematite. When the ore is heated, calcining takes place and the higher oxides of manganese dissociate to manganese oxide in the Mn_3O_4 form, which is an equal mixture of Mn^{3+} and Mn^{2+}.

Melts with compositions similar to actual plant melts and high-grade slags, as well as melts with variable basicity and CaO-to-MgO ratios, were prepared from both Mamatwan ore and synthetic materials. Silicide alloys of varying silicon content were also prepared. The melts and alloys were reacted in fine-grained low-porosity crucibles of recrystallized alumina, and a vertical molybdenum-wound resistance furnace was used to heat the ingredients rapidly to between 1500 and 1600°C. The reaction times were varied from 30s to 30 min, but equilibrium was normally found to have been reached within 15 min. The ratio of melt to alloy was also varied, and several multistage contacts were used in the investigation of optimum manganese recovery and silicon-utilization techniques. The reaction products were analysed from each group of tests.

2.2 Laboratory results

The rate of the reaction was not altered to any marked extent by either the temperature or the phase composition. However, the equilibrium state attained was greatly affected by the phase composition and the ratio of these phases. The temperature of the furnace had only a minor influence on the equilibrium conditions because of the strongly exothermic reaction. The equilibrium conditions are best expressed by distribution ratios or apparent equilibrium constants since the available fundamental thermodynamic data are not sufficient for this purpose. Thus, the following expression, originally suggested by Von Heynert and Willems [13], was used:

$$K'_{Mn,Si} = \frac{(MnO).\underline{Si}^{1/2}}{\underline{Mn}},\qquad(1)$$

Where the parentheses denote the slag phase and the underlined, the alloy phase.

The influence of the composition (basicity) of the initial melt and of the melt-to-alloy ratio on the basicity of the final slag at equilibrium (and hence the distribution ratios) is shown in Table 1, which also gives values for the apparent equilibrium constants.

Some of the results of two-stage contacts between melt, slag, and alloy are shown in Table 2. In the first stage, the manganese oxide in the slag was reduced to the minimum value by the introduction of an excess of silicomanganese. The intermediate alloy was re-used in a second stage to produce an alloy low in silicon and an intermediate slag, which was then used in a repetition of the first stage.

3. PLANT PRACTICE

In the production of medium-carbon ferromanganese at Transalloys, Mamatwan manganese ore and lime are melted in two 4 MVA open-arc furnaces. The resulting melt is subsequently reacted with a reducing agent of solid crushed silicomanganese in mixing ladles to produce an alloy with the following specifications:

Manganese:	80.0% minimum
Carbon:	1.5% maximum
Silicon:	1.5% maximum.

The lime is added to the ore to assist the melting and to increase the activity of the manganese oxide in the melt. The lime is also needed in the final slag to reduce the activity of the silica, most of which arises from the reaction. However, when the addition of lime is high, the benefits obtained may be more than out-weighed by the dilution of manganese oxide in the melt and by the associations of oxides in the slag as discussed below. Furthermore, extra electrical energy would be needed to melt a burden that has a higher mass ratio per unit of manganese. The Mn^{3+} oxidation state is lowered to Mn^{2+} in the melt by the addition of the stoichiometric amount of carbonaceous reducing agent, even though the final carbon in the alloy is raised slightly by this strategy (i.e. carbides of manganese are formed). The use of a carbonaceous reducing agent results both in a saving (a silicomanganese reducing agent is more expensive) and in the avoidance of an excessively violent reaction in the mixing ladles. The reaction temperature is lowered, which decreases refractory wear. The heat of reaction or enthalpy (ΔH) for the reaction of the Mn^{3+} is much greater than for the Mn^{2+} reaction (ΔH_{1800K} for $Mn^{3+} \rightarrow Mn^{2+} = -195.0\,kJ/mol$ and ΔH_{1800K} for $Mn^{2+} \rightarrow Mn = -50.0\,kJ/mol$) [14]. However, the liquidus temperature of the melt is raised as the Mn^{3+} is reduced to Mn^{2+}. Some bentonite is therefore added as a flux.

The basicity of the final slag is primarily a function of the basicity of the melt and the extent of the reaction. The latter is in turn a function of the amount of slag-alloy mixing, according to Bauer et al. [15]. The extent of the reaction under plant conditions is also a function of temperature, the melt-to-alloy ratio, and the amount of additional slag-forming material associated with the use of a carbonaceous reducing agent. The major constraint on the operation is that the silicon content of the final alloy must be less than 1.5%, a specification that will be met if the melt-to-alloy ratio for constant initial-phase compositions is kept to a certain minimum value. Below that value, the final alloy will be 'off grade' as a result of the relatively high residual silicon that would not have reacted.

Another constraint is that the temperature of the melt in the open-arc melting process cannot be raised above a certain value unless the composition of the melt is adjusted. If the temperature

Table 1. The influence of melt composition and melt-to-alloy ratio on the state of equilibrium [10, 11] in the laboratory tests

Melt type	CaO added %	Ratio of melt to alloy	CaO/MgO	Basicity of melt (CaO + MgO)/SiO$_2$	Basicity of final slag (CaO + MgO)/SiO$_2$	Final Si %	Distribution ratios		Apparent equilibrium constants	
							(MnO)/Mn	(SiO$_2$)/Si	K$_{MnSi}$	log K$_{MnSi}$
High-grade slag	35	5.0	7.0	7	2.97	1.3	0.471	11.46	0.042	−1.377
	35	3.0	7.0	7	2.14	1.3	0.370	16.69	0.046	−1.338
	35	2.5	7.0	7	1.76	1.5	0.254	18.67	0.024	−1.620
	35	2.0	7.0	7	1.69	4.0	0.242	7.43	0.038	−1.421
	35	1.25	7.0	7	1.61	9.0	0.206	3.52	0.049	−1.310
	35	1	7.0	7	1.54	10.8	0.170	3.16	0.043	−1.367
	35	0.83	7.0	7	1.54	12.5	0.173	2.73	0.045	−1.347
	35	0.71	7.0	7	1.55	13.9	0.185	2.43	0.054	−1.268
	35	0.63	7.0	7	1.58	15.1	0.209	2.17	0.063	−1.201
Manganese oxide melts	10	1.10	No MgO added	x	0.61	6.0	0.532	5.72	0.100	−1.000
	20	1.10		x	1.18	5.5	0.417	5.40	0.076	−1.119
	30	1.10		x	1.78	5.4	0.352	4.69	0.063	−1.201
	40	1.10		x	2.32	5.1	0.294	4.43	0.052	−1.284
	50	1.10		x	2.83	4.8	0.247	4.29	0.042	−1.377
	60	1.10		x	3.47	5.0	0.231	3.60	0.040	−1.399
Melts of lime and Mamatwan ore	0	2.0	4.5	3.46	0.67	3.0	0.47	10.0	0.082	−1.086
	10	2.0	7.9	5.66	1.01	2.8	0.39	9.71	0.066	−1.180
	20	2.0	11.6	7.85	1.45	1.9	0.35	12.74	0.048	−1.317
	30	2.0	15.4	10.04	1.89	1.5	0.32	14.53	0.039	−1.407
	40	2.0	18.8	12.24	2.30	1.3	0.30	15.23	0.034	−1.466
	0	1.54	4.5	3.46	0.62	5.4	0.46	5.61	0.107	−0.971
	10	1.54	7.9	5.66	1.00	4.5	0.38	6.27	0.080	−1.097
	20	1.54	11.6	7.85	1.36	3.7	0.32	7.19	0.061	−1.151
	30	1.54	15.4	10.04	1.59	2.8	0.27	8.86	0.045	−1.347
	40	1.54	18.8	12.24	2.06	2.6	0.24	8.81	0.039	−1.409
	0	1.43	4.5	3.46	0.60	6.5	0.42	4.94	0.108	−0.967
	10	1.43	7.9	5.66	0.95	5.9	0.34	5.15	0.082	−1.208
	20	1.43	11.6	7.85	1.29	4.3	0.28	6.58	0.058	−1.237
	30	1.43	15.4	10.04	1.64	3.8	0.24	6.87	0.047	−1.328
	40	1.43	18.8	12.24	1.93	3.6	0.22	6.70	0.041	−1.387

Table 2. A comparison of the laboratory results for three two-stage contacts between alloy and synthetic manganese oxide slags with the results for the equivalent single-stage contact to produce a similar silicon specification

Test no.	Stage no.	Melt/alloy ratio	Mn recovery %	(CaO + MgO)/SiO$_2$ Final slag basicity ratio	Si residual, %	MnO, % in final slag
1	I	1:1	76.4	1.55	10.9	13.9
	II	0.85:(1)	57.0	1.81	3.7	23.7
Net		2.0:1	66.1	–		
Single stage		2.0:1	64.4	1.69	4.0	20.1
2	I	1:1	78.0	1.54	10.8	13.4
	II	1.02:(1)	53.5	1.94	2.6	25.4
Net		2.2:1	63.6	–		
Single stage not carried out						
3	I	1:1	77.8	1.55	10.8	13.4
	II	1.37:(1)	44.5	2.03	1.2	29.4
Net		2.6:1	51.1	–		
Single stage		3.0:1	44.8	2.14	1.3	31.9

(1) Intermediate alloy

of the melt is increased by increased burden resistance, the melt-tapping temperature can be increased for a given electric-melting furnace, but prolonged open arcing towards the end of a melt results not only in a super-heated melt surface but in much cooler material in the lower part of the furnace. The size of the two melting furnaces and of the mixing ladles at Transalloys also restricts the range of melt-to-alloy ratios. Therefore, the only variable that can be adjusted to modify the basicity of the final slag is the basicity of the initial melt. Dolomite could be used instead of lime to vary the ratio of calcium oxide to magnesium oxide since 1 mol of magnesium oxide associates with 2 mol of silica (and 1 mol of calcium oxide) and thus $CaO.MgO.2SiO_2$ has a lower free-energy of reaction (ΔG) than $CaO.SiO_2$ on its own. Figure 1 illustrates the relationship between the initial and final basicities found in practice over a 6-month period at Transalloys, and typical analyses of the melt and slag produced at Transalloys are given in Table 3. The corresponding masses of the various components in the melt and the slag are also presented in Table 3, which also shows the calculated values for the resultant mass ratios of initial melt to final slag.

4. THEORETICAL CONSIDERATIONS

The initial melt is rich in Mn^{2+} and Ca^{2+} anions. There is a small quantity of Mg^{2+}, and relatively little silica and alumina. The melt is thus completely modified (i.e. free from networks), and is wholly ionic in character. The liquidus temperature of typical melts would be expected to vary between 1500 and 1600°C according to Warren et al. [16], Glasser [17, 18], Osborn et al. [19], and Riboud and Maun [20]. As the Mn^{3+} oxidation state is reduced to the Mn^{2+} state, so the liquidus temperature increases. However, the liquidus temperature of the final slag is about 150–200°C lower than that of the melt as a result of the increase in silica. The alloy has a liquidus temperature of close to 1300°C [10]. The final slag has a considerably lower basicity ratio than the initial melt, and is not modified to the extent of the initial melt, i.e., it has a partial network structure.

4.1. Changes in composition of the oxide phase during reaction

The transition from the initial melt to the final slag occurs during the reaction. The manganese oxide in the melt is lowered,
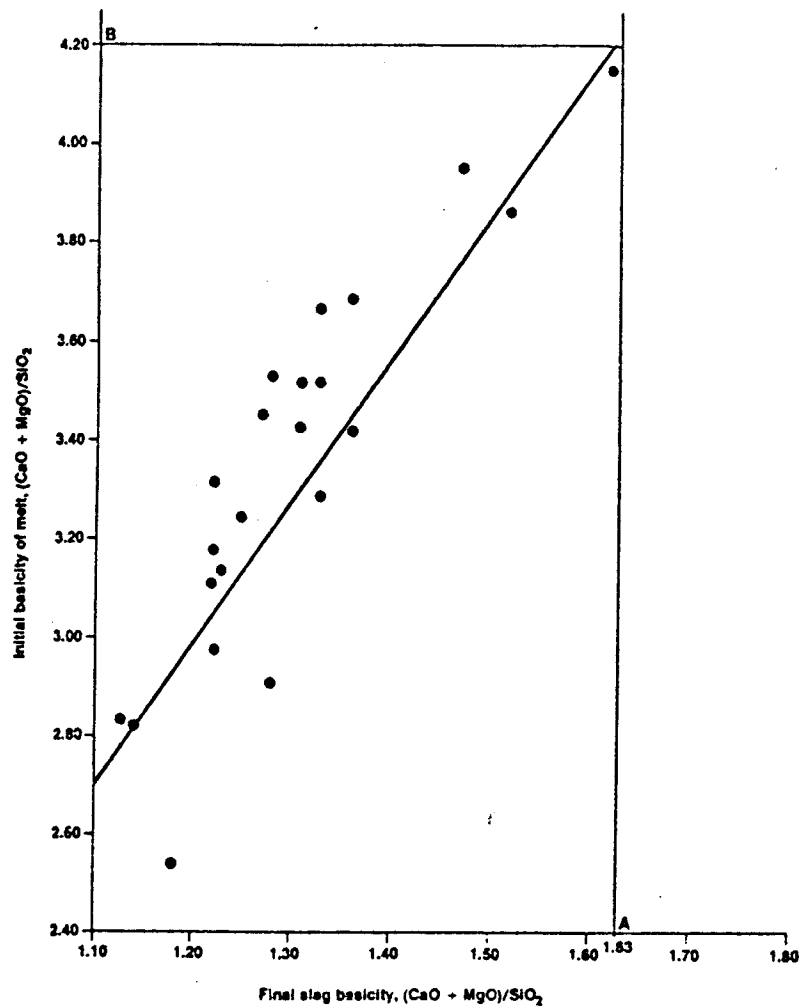

Fig. 1. The relationship between the initial basicity ratio of the melt and the final basicity ratio of the slag, based on plant data from Transalloys.

Table 3. Typical analyses of initial melt and final slag from Transalloys

Constituent	Melt		Slag	
	%	kg	kg	%
MnO	45.0	450	229	26.1
FeO	6.0	60	4	0.5
SiO₂	11.0	110	263	30.0
CaO	29.5	295	295	33.7
MgO	2.6	26	26	3.0
Al₂O₃	2.7	27	27	3.1
BaO	1.1	11	11	1.3
Available O₂	1.0	10	–	–
Others	1.1	11	20.5	2.3
Total	100.0	1000	876	100.0
(CaO + MgO)/SiO₂		2.92	1.22	

Note: The slag mass is based on the transfer of the unreduced oxides according to the following calculation:

$$\text{Slag per 1000 kg of melt} = \frac{(CaO + MgO + Al_2O_3 + BaO) \text{ in melt, kg}}{(CaO + MgO + Al_2O_3 + BaO) \text{ in slag, } \%}$$

$$= 876 \text{ kg}$$

$$\text{Ratio of melt to slag} = 1000/876 = 1.14.$$

and the silica content is increased according to the following exothermic reaction for the reduction of manganese oxide to manganese metal:

$$2(MnO) + \underline{Si} \rightleftharpoons 2\underline{Mn} + (SiO_2) \tag{2}$$
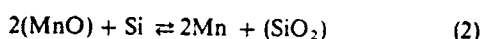
$$\Delta G_{1800K} = -30.6 \text{ J/mol Mn [14]}$$
$$\Delta H_{1800K} = -50.0 \text{ J/mol Mn.}$$

The use of silicon to reduce Mn_2O_3 (i.e. Mn^{3+}) to manganese oxide does not directly result in the production of any manganese metal. The reaction is strongly exothermic and must be contained if it becomes too violent.

The initial melt and final slag are very different in character. The composition of the initial melt and the extent of reaction determine the composition of the final slag, which can be glassy or crystalline, depending on the reaction temperature, cooling rates, or composition.

As equilibrium is approached and the silica content of the slag increases, so the concentration of the manganese oxide in the slag is lowered. Despite the presence of calcium oxide associating with the silica and thus increasing the activity of the manganese oxide, values of less than 15% manganese oxide were seldom achieved in laboratory tests except for very low melt-to-alloy ratios.

Similarly, the final alloy phase, which has a much lower silicon content than the initial alloy, is much less reactive than might be expected. This, according to Turkdogan and Hancock [21] and Tolsotoguzov [22], is because silicon deviates very negatively from Raultian ideality in the manganese–iron–silicon system.

4.2. Multistage contacting

For an alloy with the required silicon content in a single-stage contact, use has to be made of a melt that is well in excess of the amount of melt that would give the maximum manganese

recovery. This is the major limitation of a single-stage contact. In principle, a two-stage contact allows much greater flexibility because an excess of alloy can be used in the first contact to strip the slag to a low manganese oxide content (for example a slag-to-alloy ratio of 1 instead of the usual ratio of 2.5), and a high recovery of manganese will result.

This slag low in manganese oxide can be discarded, and the silicon content of the intermediate alloy will remain fairly high (9–12%). Thus, in the second stage, the alloy produced in the first stage can be contacted with a fresh melt in such a ratio as to refine the silicon in the alloy to meet the required specification of less than 1.5% silicon. The resulting slag, still rich in manganese oxide, can be re-used in a repetition of the first stage but with a slightly higher intermediate ratio of slag to alloy, or it can be used for the production of FeMnSi (silicomanganese) on an integrated ferroalloy plant such as Transalloys. The results of the two-stage laboratory tests (Table 2) demonstrate the improved overall efficiency afforded by this method: the manganese recovery is higher, and the silicon content of the final alloy is lower, for the same overall melt-to-alloy ratio.

4.3. Slag-alloy separation

A review of the thermodynamic data [23–25] indicates the existence of certain reactions or associations between the oxides in the slag phase. These slag components are presented in Table 4 in descending order of their free energies of reaction (i.e. their $-\Delta G$ values). The stoichiometric relationships shown in Table 4 for the slag-forming oxides (Al_2O_3, CaO, BaO, MgO, SiO₂ and MnO) were used in the calculation of the mass balances for all the slag components shown in Table 3. According to that calculation, the (MnO.CaO) phase will not form and there is free silica in this slag to associate with the manganese oxide according to reaction (e) in Table 4.

Table 4. The slag components expected to form* under equilibrium conditions between slag and alloy at close to 1500°C

Reaction	ΔG_{1773} kJ/mol	Reference
(a) $12\ CaO + 7Al_2O_3$ $= 12\ CaO \cdot 7Al_2O_3$	−418.6 (approx.)	23
(b) $2BaO + SiO_2$ $= 2BaO \cdot SiO_2$	−263.7	24
(c) $CaO + MgO + 2SiO_2 = CaO \cdot MgO \cdot 2SiO_2$	−154.9	23
(d) $2CaO + SiO_2$ $= 2CaO \cdot SiO_2$	−142.3	23
(e) $MnO + SiO_2$ $= MnO \cdot SiO_2$	− 25.1	24
(f) $MnO + CaO$ $= MnO \cdot CaO$	Solid solution	

* The FeO content of the slag is <0.5%, and thus the formation of $CaO \cdot FeO \cdot Fe_2O_3$
($\Delta G^\circ - 62.8$ kJ/mol^{-1}) was neglected in this study.

The presence of Al_2O_3 (from the bentonite flux) serves to tie up the calcium oxide, thereby necessitating a higher initial basicity ratio in the melt for the same degree of association between the calcium oxide and the silica in the final slag. This increases both the initial melt-to-alloy ratio and the final slag-to-alloy ratio, and the alumina is a disadvantage.

The presence of barium oxide and magnesium oxide serves to tie up silica together with calcium oxide, as shown in reactions (b), (c), and (d). As the amount of barium oxide and magnesium oxide increases, so the amount of silica 'free' to associate with calcium oxide according to reaction (d) decreases. If the amount of silica required to satisfy reactions (b) and (c) is termed the 'initial' silica, and the amount of silica required for reaction (d) is termed the 'additional' silica, then any extra silica left after these above associations can be termed the 'free' silica. The term 'critical basicity' can thus be defined for slags that would have no 'free' silica present.

It would appear that, as long as there is 'free' silica in the slag and no 'free' calcium oxide to form a complex with manganese oxide, the slag and alloy will separate readily. If the CaO/SiO_2 basicity ratio of the final slag shown in Table 3 is greater than 1.53 (($CaO + MgO)/SiO_2$ greater than 1.63 in this example), then the calcium oxide will associate with the manganese oxide, which is always present in slags associated with the production of low- to medium-carbon ferromanganese. The initial basicity of the melt in terms of the CaO-to-SiO_2 ratio should not be greater than about 4.0 and the ($CaO + MgO)/SiO_2$ ratio should not be greater than 4.2 (see Fig. 1, points A and B) if the unwanted ($CaO \cdot MnO$) association is to be avoided.

If no alumina, barium oxide, or magnesium oxide were

present in the slag shown in Table 3, a basicity ratio of $2CaO/SiO_2 = 1.86$ on a mass basis would be the critical basicity ratio [from equation (d)]. However, if no 'free' silica were present in the slag after equations (a)–(d) had been satisfied, the critical basicity ratio would be $CaO/SiO_2 = 1.44$ and the ($CaO + MgO)/SiO_2$ ratio would be 1.57, i.e. lower than if 'free' silica were present. Thus, as the quantity of 'free' silica increases, so the critical basicity ratio increases to a maximum of 1.86.

A critical basicity value can therefore be determined for any given alumina, barium oxide, and magnesium oxide contents. The lowest, and thus the least-favourable, basicity would occur if only reactions (b) and (c) were satisfied. The highest and most-favourable, basicity ratio would occur if neither barium oxide nor magnesium oxide were present in the slag and the only reaction was (d).

In practice, the final separation of metal and slag occurs while the metal is being poured into the casting beds. Slag temperatures at this stage are expected to be in the region of 1350–1450°C, based on a series of measurements at Transalloys with a hand-held Mikron 57 i.r. pyrometer. With initial melt basicities of more than 4.20 (i.e. final slag basicities greater than 1.63), plant practice has shown that the separation of alloy and slag tends to become difficult. This finding coincides with a situation in which the formation of $MnO.SiO_2$ in slag as detailed above is not possible because of an excess of the basic oxides barium oxide, magnesium oxide, and calcium oxide, resulting in the formation of an $MnO.CaO$ phase.

The Transalloys slag described in Table 3 can be reconstituted to obtain various silica contents (i.e. simulating a range of degrees of manganese recovery) as shown in Table 5.

Table 5. The relationship between the silicon content of the slag and the critical basicity ratio

	$SiO_2\%$	*Normal basicity ratio		*Critical basicity ratio		Ratio of free SiO_2 to SiO_2 for reactions (b) (c) and (d)
		(CaO/SiO_2)	$(CaO + MgO/SiO_2)$	(CaO/SiO_2)	$(CaO + MgO/SiO_2)$	
Increasing extent of reaction	20	1.92	2.09	NA	NA	−0.25†
	22	1.71	1.86	NA	NA	−0.16†
	24	1.52	1.66	NA	NA	−0.05†
	25	1.44	1.57	1.44	1.57	0
	30	1.12	1.22	1.53	1.63	0.28
	35	0.89	0.97	1.60	1.68	0.60

* The normal basicity ratio is based on the original CaO/SiO_2 or ($CaO + MgO)/SiO_2$ ratio where no extra CaO has been added. The critical basicity ratio is then determined for the given slag by an increase in the CaO level while all the other components are kept constant
† Hypothetical values
NA Not applicable

These values are plotted in Fig. 2, which shows the influence of recovery (i.e. increasing silica in the final slag) and increasing basicity (CaO/SiO_2) on the critical basicity ratio. The boundary line in Fig. 2 indicates the existence of the two slag types. The lower-basicity slags (silica greater than 25% and below the critical basicity line) contain an $MnO.SiO_2$ complex and excess uncomplexed or 'free' MnO. The higher-basicity slags (silica less than 25%, and greater than 25% when above critical basicity) contain an ($MnO.CaO$) complex and excess uncomplexed MnO. The slag with a silica content of 25% contains the minimum silica requirement to satisfy equations (b), (c) and (d) completely, i.e. there is zero 'free' silica. Hence, if the silica is less than 25%, or if the critical basicity is exceeded as shown in the shaded area, then 'free' calcium oxide is available to form ($CaO.MnO$), satisfying equation (f) and slag–alloy separation becomes a problem. In addition, there is unnecessary dilution of manganese oxide by calcium oxide in this region.

The normal slags in the production of medium-carbon ferromanganese at Transalloys have a silica content of 25–35%. This indicates that a (CaO/SiO_2) basicity below 1.44 at 25% silica, or 1.53 at 30% silica, will ensure the formation of $MnO.SiO_2$ in the slag (see Fig. 2). For optimum conditions, operations should thus aim at a basicity just below the critical value, and the 30–35% silica region is most suitable. Plant experience has also shown that slag–alloy separation often becomes a problem when the slag has a manganese oxide content of over 30%. Closer inspection of the data reveals that slags high in manganese oxide also have basicity ratios higher than 1.40 as a result of incomplete reaction (i.e. insufficient

silicon transfer from alloy to slag). It is therefore prudent to allow a safety margin of operation below the critical basicity to allow for incomplete reactions, but, at the same time sufficient calcium oxide should be added to the initial melt to ensure sufficiently good recoveries. Thus, there is an optimum balance.

A further consideration regarding the problem is that the crystalline nature of the slag might also be responsible for difficulties in slag–alloy separation since the laboratory tests showed that glassy slags separated much more easily from the alloy than more crystalline slags. Variations in temperature, cooling rate, and composition are the usual cause of the different slag forms.

Surface tension is probably also a contributory factor since increasing basicity results in lower surface tension in the slag phase [26]. The slag–alloy interfacial tension would also be affected by the basicity of the slag, and increased difficulty of separation might therefore be expected at higher basicities.

5. DISCUSSION

5.1. Equilibrium relationships

The results obtained in the laboratory and those achieved at the plant are best compared by a consideration of the respective apparent equilibrium constants. Distribution ratios and apparent equilibrium constants were calculated for the final slags and product alloys from plant data collected over a 6-month period at Transalloys. Normal plant operation corresponds to a melt-to-alloy ratio of approximately 2.5 to 1.
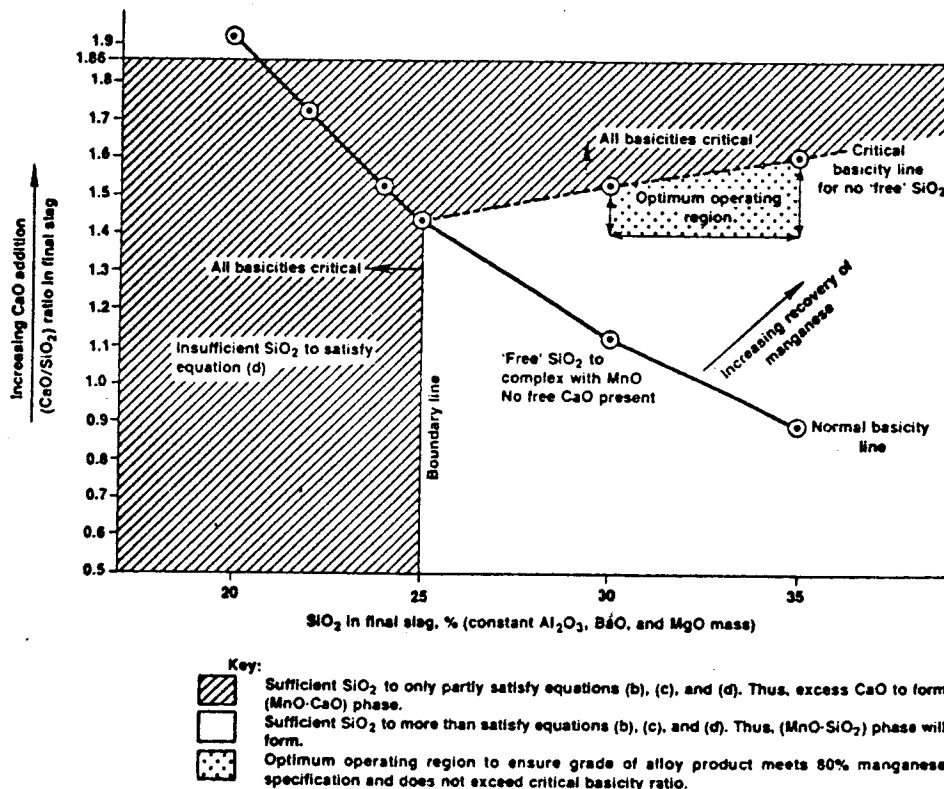

Fig. 2. The relationship between the final CaO/SiO_2 ratio and the SiO_2 content of the slag in terms of 'free' SiO_2 and 'free' CaO.

Similar ratios were used by Barcza [10] and Channon [11], although both lower and higher ratios were also used extensively in their laboratory tests, in which greater flexibility was possible. The CaO-MgO ratio in the melt, and thus also in the slag, is reasonably constant in plant practice at 11-1, although a range of CaO-MgO ratios was investigated by Barcza [10] and Channon [11] as shown in Table 1.

Figure 3 shows the graph of $\log K'_{Mn,Si}$ against the basicity ratio of the final slag for the plant and laboratory results. The plant data used in the plotting of the results shown in Fig. 3 are those in Table 6. The starting material at Transalloys consisted of a melt of Mamatwan manganese ore and lime, in which the manganese oxidation state was Mn^{2+} (i.e. MnO) and the reducing agent was silicomanganese with a silicon content of about 16%. The materials used in the laboratory tests consisted of a melt (either synthetic or based on Mamatwan ore) in which the manganese oxidation state was normally half Mn^{3+} and half Mn^{2+} (i.e. Mn_3O_4), and an alloy of silicomanganese normally containing 22% silicon.

The differences between the melt and the alloy used at Transalloys and those used in the laboratory tests are

Fig. 3. The plot of $\log K'_{Mn,Si}$ against the basicity ratio at equilibrium for several plant and laboratory slags.

responsible for the plant values for $\log K'_{Mn,Si}$ being more negative than the values obtained in the laboratory. The explanation for the difference in $\log K'_{Mn,Si}$ was that extra silicon from the alloy is consumed in reducing the Mn^{3+} to Mn^{2+} in the laboratory tests, and hence the basicity ratio of the melt decreased before any manganese was recovered [see equation (3)]:

$$2(Mn_2O_3) + 3Si = 4Mn + 3(SiO_2) \qquad (3)$$
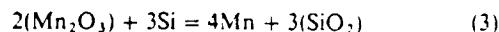
$$\Delta G_{1800K} = -175.2 \, kJ/mol \quad [14]$$
$$\Delta H_{1800K} = -195.0 \, kJ/mol.$$

Nevertheless, the final (MnO)-Mn ratios are fairly similar in both the plant and the laboratory systems. However, the second and major difference is the silicon content at equilibrium: the plant values are invariably lower than those obtained in the laboratory (see Tables 1 and 6). The (SiO_2)-Si ratios for the plant slags ranged from about 20 to 200, whereas those in the laboratory varied between 2 and 20. Although the basicity ratio of the laboratory melt was higher than that on the plant, the final slag basicity was somewhat lower because the Mn^{3+} was reduced by silicon, and not by carbon. The initial silicon content of the alloy used in the laboratory tests was also higher, namely 22% compared with that of 16% in the plant alloy. The final silicon content in the laboratory alloys was thus slightly higher than those associated with plant practice at Transalloys, despite the silicothermic reduction of Mn^{3+} in the laboratory tests.

It therefore appears that, in the laboratory tests, reaction (3) reached the given equilibrium state as a function of the basicity ratio and manganese oxide content of the slag, rather than as a function of the silicon in the alloy. This conclusion explains the higher residual silicon in the laboratory alloy product despite the extra silicon consumed for reaction (3), and therefore the less negative $\log K'_{Mn,Si}$ values. Thus, the higher initial basicity ratios of the laboratory melts compared with those of the plant melts gave rise to lower final basicity ratios in the laboratory slags than in the final plant slags, but the initially higher silicon contents in the laboratory alloys remained higher in the final laboratory alloys than in the plant alloys.

5.2. Critical basicity ratio

Most of the plant slags fall below the critical basicity ratio (CaO + MgO)/SiO_2 of 1.63. The recovery of manganese and the utilization of silicon cannot be increased above the optimum basicity value. The results of Barcza [10] and Channon [11] show that a maximum recovery value or point is reached close to this basicity, and a single-stage contact thus has obvious limitations despite the choice of the optimum melt composition.

5.3. Multistage contacting

In the overall optimization of the process using a multistage approach, the constraint of the critical basicity ratio, especially in the second stage where a higher final basicity results, must be taken into consideration.

In plant practice, it is imperative that a reasonable proportion of the alloy should be added in the second stage of a two-stage contact. The basicity ratios resulting from the second stage of the laboratory-scale tests where the melt-to-alloy ratio in the first stage was 1 to 1, were in the range 1.74 to 2.03. These values are
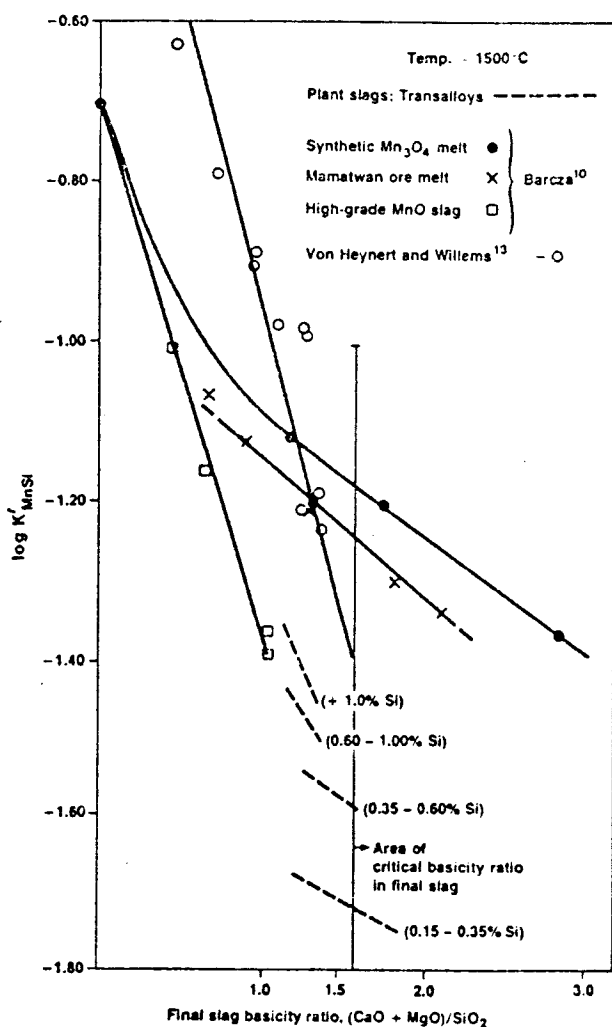
Table 6. Plant data from Transalloys over an operating period of six months

Si range in product	Final basicity ratio (CaO + MgO)/SiO₂	Si %	(MnO)/Mn ratio	(SiO₂)/Si ratio	Melt/alloy ratio	K$_{Mnsi}$	log K$_{Mnsi}$	No. of data points
0.15 to 0.35% Si	1.33	0.26	0.40	123.1	2.32	0.0204	−1.691	10
	1.29	0.21	0.41	148.1	2.82	0.0188	−1.726	11
	1.36	0.20	0.41	131.0	2.44	0.0183	−1.737	9
	1.47	0.15	0.37	199.0	2.82	0.0143	−1.844	10
	1.52	0.23	0.40	112.6	2.62	0.0192	−1.717	12
	1.22	0.23	0.36	128.7	2.50	0.0173	−1.763	8
	1.76	0.20	0.42	112.0	3.12	0.0188	−1.726	9
	1.62	0.30	0.33	88.0	3.12	0.0181	−1.743	11
	1.22	~0.25	0.38	129.0	2.78	0.0190	−1.721	1
	1.29	~0.25	0.41	136.0	2.78	0.0205	−1.688	1
	1.33	~0.25	0.41	131.0	2.78	0.0205	−1.688	1
	1.40	~0.25	0.40	123.0	2.78	0.0200	−1.699	1
	1.48	~0.25	0.40	113.0	2.78	0.0200	−1.699	1
	1.60	~0.25	0.33	88.0	2.78	0.0165	−1.783	1
0.35 to 0.60% Si	1.33	0.41	0.36	70.0	2.32	0.0231	−1.637	9
	1.35	0.48	0.41	62.5	2.97	0.0284	−1.547	10
	1.36	0.55	0.39	55.6	2.82	0.0289	−1.539	7
	1.22	0.55	0.36	73.1	2.55	0.0267	−1.574	10
	1.25	~0.50	0.36	53.0	2.63	0.0255	−1.594	1
	1.32	~0.50	0.41	60.0	2.63	0.0290	−1.538	1
	1.41	~0.50	0.39	53.0	2.63	0.0176	−1.559	1
	1.55	~0.50	0.36	68.0	2.63	0.0255	−1.594	1
0.60 to 1.00% Si	1.27	0.77	0.36	37.8	2.97	0.0316	−1.500	8
	1.25	0.91	0.38	32.2	3.57	0.0362	−1.441	11
	1.18	0.91	0.40	32.0	2.62	0.0382	−1.418	7
	1.13	0.99	0.36	32.0	2.28	0.0358	−1.446	7
	1.30	0.95	0.36	30.7	2.59	0.0351	−1.455	7
	1.31	0.95	0.35	30.8	2.75	0.0341	−1.467	6
	1.31	0.82	0.35	35.7	2.03	0.0317	−1.499	9
	1.14	0.91	0.35	34.2	2.50	0.0334	−1.476	9
	1.32	0.90	0.34	32.7	2.45	0.0323	−1.491	9
(+ 1.00% Si)	1.28	1.16	0.34	25.9	3.06	0.0366	−1.436	6
	1.24	1.23	0.34	25.1	2.99	0.0377	−1.424	7
	1.23	1.33	0.34	22.8	2.69	0.0392	−1.407	7
	1.33	1.18	0.30	25.3	2.59	0.0326	−1.487	6
	1.22	1.20	0.32	25.4	2.36	0.0351	−1.455	9
	1.22	1.64	0.33	18.8	2.00	0.0422	−1.374	6
	1.22	1.14	0.33	27.5	2.25	0.0352	−1.453	8
	1.28	1.07	0.36	27.8	2.58	0.0372	−1.429	7
	1.33	1.23	0.33	24.1	2.51	0.0366	−1.437	7

greater than the critical basicity ratio (CaO + MgO)/SiO₂. Even for single-stage contacts, in which high melt-to-alloy ratios are used, basicity ratios above the critical value can result (see Table 2). Thus, to achieve the optimum conditions, the optimum melt-to-alloy ratio should be used during both reaction stages. To determine the optimum split between the alloy used in the first and second stages, it is recommended that further laboratory work should be carried out. Calculations of the theoretical split of melt-to-alloy ratios in a two-stage process indicate that the optimum ratios should be about 1.5 and 1.0 for the first and second stages respectively. At the time of the laboratory-scale tests, the industrial problem of a critical

basicity ratio and the slag–alloy separation problem had not been identified. Hence, this additional constraint was not taken into account when the range of melt–alloy ratios to be studied in the multistage part of the laboratory work was selected.

A rather interesting practical approach to this problem of optimum conditions would be the use of a high proportion of moderately high-grade manganese oxide slag to the silicomanganese alloy. The manganese oxide units are cheaper than silicon units, and this bias would ensure that the final low-carbon ferromanganese alloy met the specification. The low recovery of manganese would not be too serious. Hot-tapped high-grade slag (with a manganese content of 35–40%) should

be reacted with hot silicomanganese (to ensure sufficient heat), and a holding furnace would therefore be required for the alloy. The low-grade slag (with a manganese content of 20–25%) produced during the production of high-carbon ferromanganese using calcium-rich ores like those in South Africa is possibly not ideally suited to such a process since its content of manganese oxide is too low.

6. SUMMARY

(1) The major competitor to low- to medium-carbon ferromanganese is electrolytic manganese, and the alternative technique to slag-alloy contacting is the decarburization of high-carbon ferromanganese by blowing with oxygen and steam.

(2) An examination of plant and laboratory data for melts, slags, and alloys associated with the production of low- to medium-carbon ferromanganese shows that, if optimum conditions are to be achieved, several variables have to be carefully controlled. These include the following: (a) melt composition, (b) alloy composition, and (c) melt-to-alloy ratio in single or two-stage contacts.

(3) The basicity ratio of the slag has to be kept below the critical value. The critical basicity ratio that can be tolerated decreases as the amounts of alumina, barium oxide, and manganese oxide increase, and the use of bentonite clay as a flux in the melting of the ore is therefore not recommended. The use of manganese ores with high contents of barium oxide is not advisable. Final slag-alloy separation problems are expected above the critical basicity ratio.

(4) The composition of the initial alloy is not as critical as that of the slag, but the silicon content must be determined before the melt-alloy ratio is optimized. This ratio must be controlled so that the resulting alloy will have a silicon content of less than 1.5% and the slag will have a basicity below the critical value.

(5) Multicontacting of the melt and alloy can result in better recoveries of manganese and alloys very low in silicon. However, the tolerance with respect to critical basicity is a restriction that must be carefully observed in the second or refining stage. This imposes limitations on the minimum melt-alloy ratio that should be used during the first stage.

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