

# PREPARATION OF PRE-REDUCED BRIQUETTES AND STUDIES ON THE KINETICS OF THE PROCESS UNDER REDUCED PRESSURE

A. K. TRIPATHY \*

S. C. KORIA \*\*

& M. N. SAXENA \*\*\*

## Abstract

**I**NVESTIGATIONS has been carried out to find the optimum conditions for the production of highly reduced iron ore briquettes suitable as a blast furnace feed from Indian ore fines and low grade coke/wool charcoal under reduced pressure  $1 \times 101$  mm. (Hg.) The effects of time (1/4 hr. to 6 hr.) temperature (950°C to 1150°C and  $Fe_2O_3/C$  ratio (1/3 to 1/5) on the rate of reduction of iron ore briquettes have been studied. From the kinetic results, a mechanism for reduction of iron oxide in iron ore briquettes is proposed and optimum conditions for production of highly reduced iron ore briquettes are summarised.

## Introduction

In recent years, a large number of significant developments have taken place in the technology of iron making including oxygen enrichment, humidification of the blast, higher blast temperatures, fuel injection through tuyeres and employment of high top pressure. It has been realised that by using partially reduced pellets or briquettes, the coke rate can be decreased and capacity of the furnace can be considerably increased. Republic Steel Company of U.S.A. has reported (1) 9 per cent increase in production and 11.3 per cent decrease in coke rate by charging metallised briquettes (71 per cent Fe and 84 per cent metallisation) comprising 14 per cent of the total charge. In Japan, at Hegachida Plant at Yawata(2), it has been possible to increase the production and decrease the coke rate each by about 18 per cent by charging pre-reduced pellets (69 per cent Fe, 58 per cent metallisation) amounting to 40 per cent of the total charge. In the experimental blast furnace at Bruceton, U.S.A.(3), 24 per cent increase in production and 19 per cent decrease in coke rate have been reported by charging 397 kg. metallised iron powder (98.7 per cent Fe and 98 per cent metallisation) per ton of hot metal. In addition to the above mentioned advantages, the use of pre-reduced pellets or bri-

quettes is further justified in view of the scant reserves of good quality coking coal and utilisation of large quantity of ore fines resulting from mechanised mining.

India has vast reserves of iron ore (27,270 million tons)(4) with average iron content around 56 per cent but due to their soft nature, the ore fines are as high as 40 per cent of the total ore mined. In contrast, metallurgical grade coking coal reserves (5) of good quality are only 1600 million tons. After washing and blending, about 3000 million tons can be used for iron smelting. With the anticipated (5) demand of 23 million tons of coking coal in the steel plants in 1973-74, the reserves will last for about 70-80 years. The total reserves of non coking coal including lignite coke are estimated and reported (6) to be around 103,000 million tons. These low grade solid fuels can not be used in the blast furnaces because of their soft nature, poor strength and quality. It is therefore, high time to develop economic methods for the utilisation of ore fines and low grade solid fuels. Moreover, the existing blast furnaces are able to cope with the requirements of the country for iron and steel. Therefore, it is essential to increase the capacity of the existing blast furnaces by using pre-reduced briquettes with the regular charge.

\* Research Scholar, I.I.T., Bombay.

\*\* Lecturer, Deptt. of Metallurgical Engineering, University of Roorkee, U. P.

\*\*\* Professor & Head, Deptt. of Metallurgical Engineering, University of Roorkee, Roorkee, U. P.

Work so far reported (7-11) in literature is mainly concerned with studies on kinetics of reduction of pure iron oxide using activated charcoal. Not much work has been reported (12,13) regarding the use of iron ore and low grade solid fuels like charcoal, low grade coke, lignite coke etc. The present investigation has been undertaken with a view to arrive at optimum conditions for the preparation of highly reduced iron ore briquettes with good mechanical strength by using Indian ore fines and nonmetallurgical solid fuels like low grade coke and wood charcoal. The influence of reduction time, temperature and  $Fe_2O_3/C$  ratio under reduced pressure on the reduction rate of iron ore briquettes have been investigated. From the kinetic results obtained in these studies, a mechanism for the reduction of iron oxide in the iron ore briquette by a solid reduction has been proposed.

## EXPERIMENTAL WORK

### Materials used

The iron ore fines used in this investigation were obtained from Gua mines and contained 85 per cent  $Fe_2O_3$  and 15 per cent gangue. The loss on ignition was 7.8 per cent. The particle size of the fines used was in the range - 100 to + 150 mesh.

The solid reductants employed in this study were low grade coke and wood charcoal, both procured from local markets of Roorkee. Wood charcoal was crushed and heated in an inert atmosphere at  $900^\circ C$  for 1 hr. to remove volatile matter. The size fractions of reductant used for reduction experiments were in between -100 to + 150 mesh. The proximate analysis in wt. per cent of these two reductants is given in table-1.

**Table-1**  
Proximate analysis of reductants

Type of reductant	%Moisture	%ash	%Volatile matter	%Fixed Carbon
Low grade coke (As received)	0.92	29.47	4.86	64.93
Wood Charcoal (Treated)	1.2	14.8	4	80

The ore fines and powdered reductant of the same mesh size were mixed thoroughly in a rotating cylinder for 8 hours. The proportion of iron oxide in iron ore to carbon was varied from mixture to mixture. The mixture  $Fe_2O_3 + 3C$  investigated thoroughly was prepared by mixing 3 g. atoms of carbon to 1 g. mole of  $Fe_2O_3$ . Other mix-

tures such as  $Fe_2O_3 + 3.5C$ ,  $Fe_2O_3 + 4C$ ,  $Fe_2O_3 + 5C$  were also prepared to study the effect of  $Fe_2O_3/C$  ratio on the kinetics of reduction.

For the reduction experiments, samples weighing 6 gms were taken from the prepared mixtures. This mixture was compacted under a pressure of 470 Kg/sq cm in a universal testing machine using a dia of 1.5 cm. The length of the briquettes varied between 2 to 2.54 cms. The briquettes thus prepared were first air dried and then kept in an oven at  $120^\circ C$  for about 24 hrs to remove moisture completely.

Reduction experiments were carried out in one end closed 2.54 cm. dia by 56 cm. long alumina tube which was kept horizontally in a kanthal wound 5 cm. dia resistant furnace. The open end of the reaction tube was closed with a solid rubber cork and connected to vacuum pump. The evacuation achieved was of the order of  $1 \times 10^{-1}$  mm. of mercury. Using a calibrated Pt-90 Pt-10 Rh thermocouple, the temperature profile along the length of the reaction tube was determined; it was found to be uniform (plus or minus  $2^\circ C$ ) over a 4" long zone from the closed end.

Two dried and weighed briquettes of the same mixture were kept at a time on the fireclay boat and then this boat was transferred to the alumina reaction tube. The tube was then evacuated to  $10 \times 10^{-1}$  mm. of Hg. It was inserted in the furnace which was maintained at the desired temperature. The furnace temperature was kept  $5^\circ C$  higher than required as this was found to be the temperature difference between the inside and outside of the reaction tube. Usually 2 to 3 minutes elapsed before the samples attained the temperature of the surroundings. After the reduction was carried out under isothermal conditions for a pre-determined length of time, the reaction tube was taken out and cooled to room temperature under vacuum. Then the vacuum seal was broken and the briquettes were taken out, weighed and analysed for residual carbon by the usual Strohlein apparatus.

The percentage reduction of iron oxide in the briquette was calculated on oxygen basis. Let W be the weight loss after reduction, x be weight of carbon removed, y be weight of oxygen removed, z be the weight of volatile matter removed and w be the weight loss on ignition of iron ore then

$$W = x + y + z + w$$

$$Y = W - (x + z + w)$$

If  $Y_T$  be the oxygen removable, then

$$\text{percent reduction} = \frac{y}{Y_T} \times 100$$

In this way, the influence of time (upto 300 mts) temperature (950 to 1150°C) and  $\text{Fe}_2\text{O}_3/\text{C}$  ratio on the rate of reduction by both low grade coke and treated wood charcoal was studied.

## RESULTS AND DISCUSSION

### A. Studies on the kinetics of reduction

The percentage reduction of iron oxide in the briquettes consisting of iron ore and low grade coke or wood charcoal at constant  $\text{Fe}_2\text{O}_3/\text{C} = 1/3$  ratio after different intervals of time under reduced pressure ( $1 \times 10^{-1}$  mm. of Hg) for

various temperatures 950 degrees Centigrade, 1050 degrees Centigrade, 1100 degrees Centigrade and 1150 degrees Centigrade are plotted in fig. 1 and 2. From these plots, the marked influence of temperature on reduction of iron oxide particularly in the initial stages (upto 30 mts.) is quite conspicuous. Further, percent reduction (R) is not directly proportional to the time (t) of reduction. For example, percent reduction of iron oxide in iron ore-low grade coke briquettes for a period of 90 minutes increases from 40 per cent at 1000°C to 92 per cent at 1150 deg. C. Similar observation can also be made from fig. 2.

The plots obtained in fig. 3 and 4 in both the cases confirm the following relationship

$$R = c \log t + x$$

Where  $c$  and  $x$  are constants,  $R$  indicates

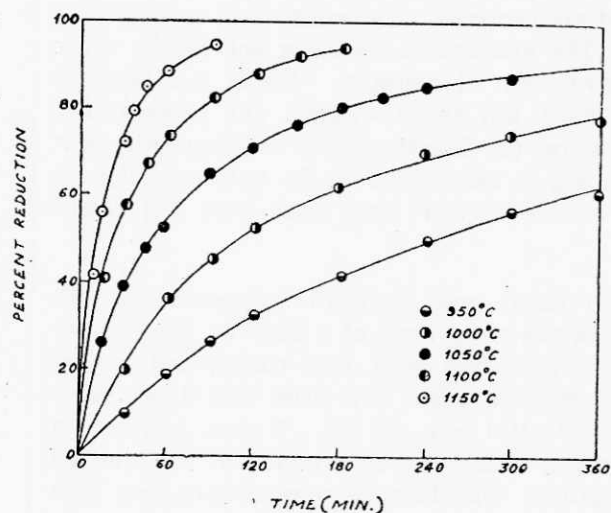


Fig. 1. Effect of temperature on reduction reaction  $\text{Fe}_2\text{O}_3 + 3\text{C}$  (using wood charcoal).

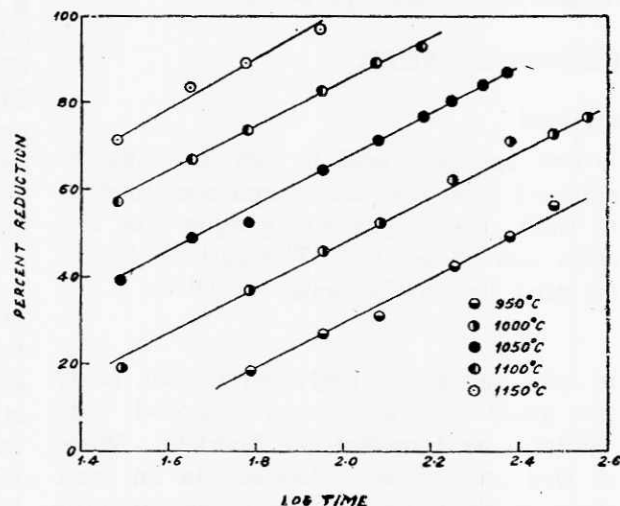


Fig. 3 Percent reduction vs log time plots (using wood charcoal).

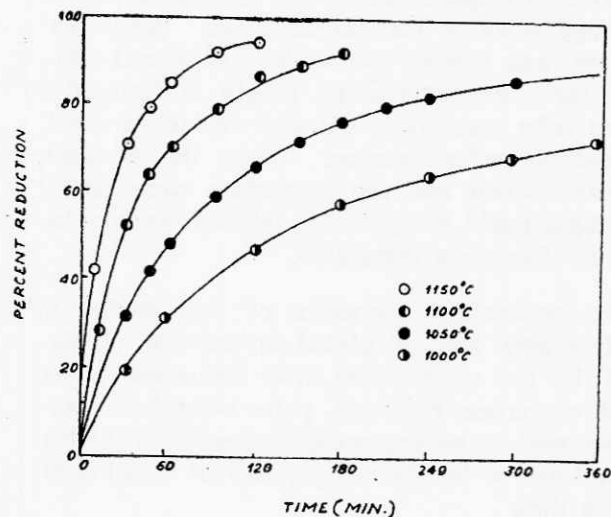


Fig. 2 Effect of temperature on reduction reaction  $\text{Fe}_2\text{O}_3 + 3\text{C}$  (using low grade coke).

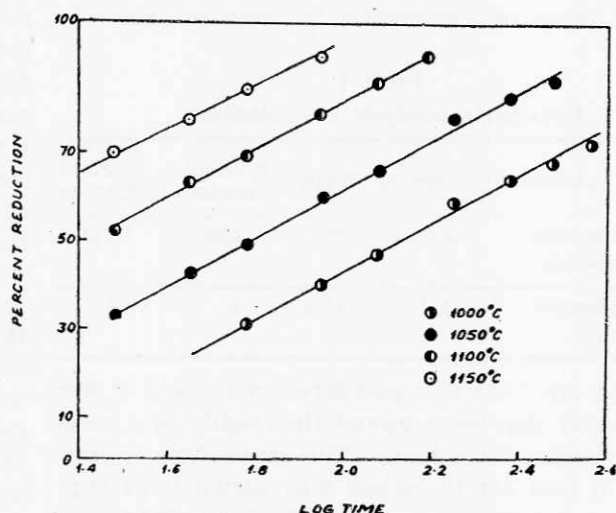


Fig. 4 Percent reduction vs log time plots (using low grade coke)

percentage reduction and  $t$ , the time of reduction. In this presentation, for purposes of analysing the kinetic results by semi log plot one or two initial values of reduction percent have not been considered as they have been found to be highly time sensitive. For example, using wood char-

coal as reductant, present reduction at  $1050^{\circ}\text{C}$  was found to be 45 per cent in 15 minutes. The values of  $c$  vary from 53 to 55 for low grade coke and 50-58 for wood charcoal. In this range, the activation energy of the reduction process has been calculated in a way similar to the one

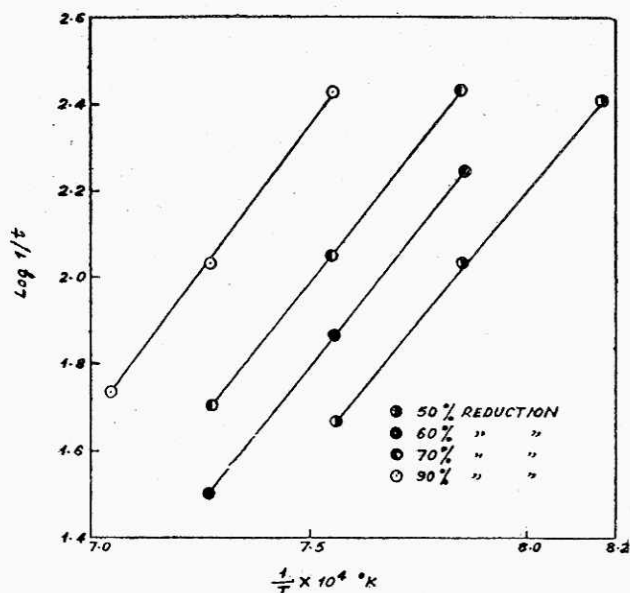


Fig. 5 Log  $1/t$  vs  $1/T \times 10^4$  ( $^{\circ}\text{K}$ ) for different percentages of reduction (using wood charcoal)

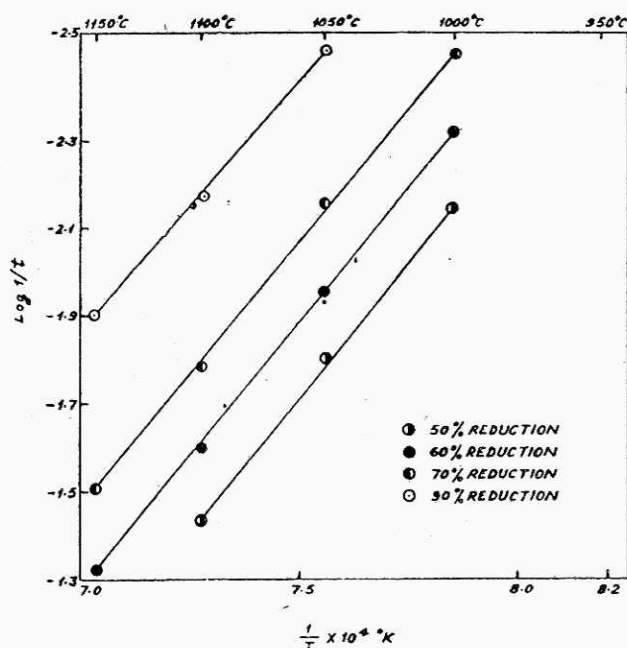


Fig. 6 Log  $1/t$  vs  $1/T \times 10^4$  ( $^{\circ}\text{K}$ ) for different percentages of reduction (using low grade coke).

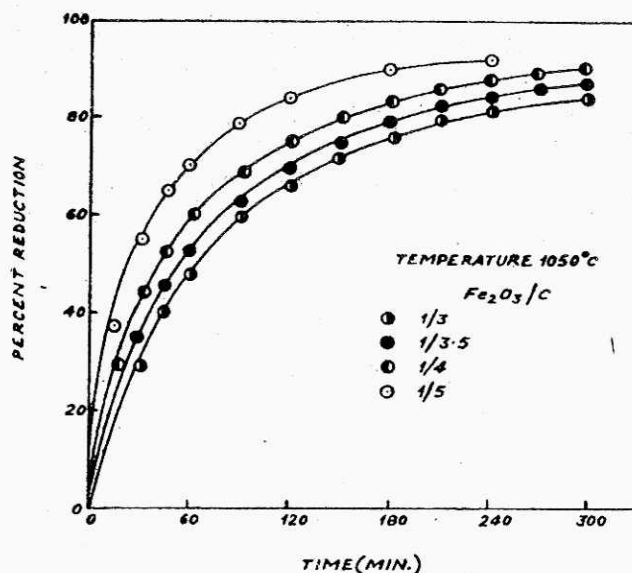


Fig. 7 Effect of  $\text{Fe}_2\text{O}_3/\text{C}$  ratio on percent reduction (using wood charcoal)

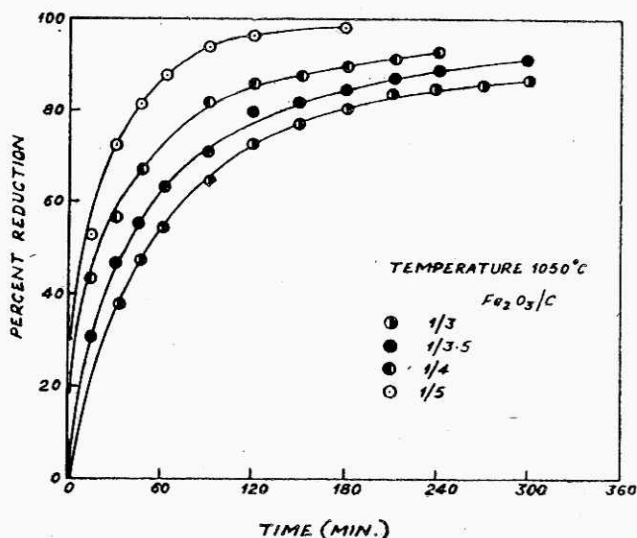


Fig. 8 Effect of  $\text{Fe}_2\text{O}_3/\text{C}$  ratio on percent reduction (using low grade coke)

atures, the reciprocal of time for attaining a de-  
 cording to Arrhenius relationship at all temper-  
 entiating R with respect to t in equation (1), it  
 adopted by Jena and coworkers (14). By differ-  
 is observed that the rate  $dR/dt$  is proportional to  
 $1/t$ , reciprocal of time of reduction. Hence ac-  
 finite reduction should be proportional to  $e^{-E/RT}$   
 where E, R and T are activation energy, gas con-  
 stant and absolute temperature respectively.  
 The log  $1/t$  vs  $104 T^{\circ}K$  graphs for low grade  
 coal and wood charcoal reductants at different  
 reduction percentages are plotted in fig. 5 and 6  
 respectively. From their slopes, the activation  
 energy values have been calculated and found to  
 be equal to 53.9 and 57.2 Kcal/g. mole for iron  
 ore reduction with low grade coke and wood  
 charcoal respectively.

From the results reported above, it is seen  
 that during initial stages of reduction (upto 30%),  
 the reaction rate is relatively very high. This  
 may be due to the surface reaction between re-  
 actants. After 30 per cent reduction, the results  
 obey the linear relationship (1) which suggests  
 that the process is controlled by diffusion. The  
 activation energy values found in case of low

grade coke (53.9 Kcal/g. mole) and wood char-  
 coal (57.2 Kcal/g. mole) are in close agreement  
 with the reported value (15) (55 Kcal/mole) for  
 the diffusion of iron through  $Fe_2O_4$ . Hence, it  
 is suggested that diffusion of iron through  $Fe_3O_4$   
 is the most probable rate determining step of  
 90 per cent reduction.

Beyond 90 per cent reduction, the reaction  
 became extremely sluggish owing to poor availa-  
 bility of reactants.

#### B. Effect of $Fe_2O_3$ ratio

Experiments were conducted using the  
 same mesh size of iron ore and low grade coke  
 or wood charcoal as the reducing agents. The  
 $Fe_2O_3/C$  ratio was varied between 1/3, 1/3.5,  
 1/4 and 1/5

It is discernible from the results shown in  
 fig. 7 and 8 that as the ratio is decreased, the  
 rate of reduction increases considerably. In other  
 words reduction proceeds much more rapidly in  
 mixtures with proportionately higher carbon  
 content. The time-span data for half complete  
 reduction for the reductants low grade coke and  
 wood charcoal are given in table 2 & 3.

TABLE II

Effect of  $Fe_2O_3/C$  ratio on time-span (T/2) Value for low grade coke as reductant

Mixture	$Fe_2O_3/C$ ratio	Time for half complete reduction (Min)				
		50°C	1000°C	1050°C	1100°C	1150°C
$Fe_2O_3 + 3C$	1/3	480	150	66	30	15
$Fe_2O_3 + 3.5C$	1/3.5	430	120	54	25	12
$Fe_2O_3 + 4C$	1/4	360	90	42	20	10
$Fe_2O_3 + 5C$	1/5	300	60	27	10	—

TABLE III

Effect of  $Fe_2O_3/C$  ratio on time-span (T1/2) values for wood charcoal as reduction

Mixture	$Fe_2O_3/C$	Time for Half complete reduction (Min)				
		950°C	1000°C	1050°C	1100°C	1150°C
$Fe_2O_3 + C$	1/3	240	120	48	25	15
$Fe_2O_3 + 3.5C$	1/3.5	210	90	33	20	13
$Fe_2O_3 + 4C$	1/4	180	75	21	20	10
$Fe_2O_3 + 5C$	1/5	60	30	12	5	—

### Conclusions

1. The effect of temperature on the degree of reduction of iron ore fines was found to be pronounced throughout the range of temperatures studied. It is possible to produce metallic iron from iron ore only above 1000°C.

2. In the sequence of reduction of iron ore to metallic iron, two stages were observed. Initial stage of reduction was found to be controlled by surface reaction while during the later stage diffusion of iron through  $Fe_3O_4$  appears to control the reaction.

3. Reduction rate was found to be higher in mixtures with proportionately higher carbon content.

### References

1. Dastur et. al, Trans. IIM, Vol. 21, June 1968, P. 92.
2. Takeda K., Blast furnace and Steel plant. Vol. 56, 1968, p. 297.
3. Woolf, Jr. of Metals, Vol.8, Feb. 1966, p. 243.
4. Balsundaram M.S., Eastern Metals Review, Annual No. April, 1972, p. 39.
5. Altekar V. A. et. al, Paper presented in 25th Annual Technical Meeting of IIM, Feb. 1972 held in Delhi.
6. Chatterjee A.B, NML Tech. Jr., Vol. 11, No. 4, 1969, p. 4.
7. Rao Y. K., Met. Transaction, Vol. 2, May 1971, p. 1439.
8. Yun T. S., Transaction of the ASM, Vol. 54, 1961, p. 129.
9. Bankloh W. and Durer R., Arch Eisenhüttenw, Vol. 5, 1931, p. 455.
10. Benkloh W. and Zimmermann G., Stahl und Eisen, Vol. 53, 1933, P. 172.
11. Rao Y. K., Paper presented at annual meeting of AIME, at New York, Feb. 25 1968.
12. Baldwin B. JISI, Vol. 179, 1955. p. 179.
13. Kapoor A. N. et. al., Paper presented at IIM Symposium, Dec. 1970.
14. Jena et. al. Jr. of less Common Metals, Vol. 10, 1966, p. 185.
15. Kubaschewski and Hopkins, Oxidation of Metals and Alloys 2nd edition, p. 33.