A New Equation for the Cr Equivalent in 9 to 12 Pct Cr Steels

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In advanced 9 to 12 pct Cr steels, the Cr equivalent is used as a measure to check the formation of δ -ferrite. In the present analysis, 29 alloys of varying composition were vacuum induction melted, and the amounts of δ -ferrite were measured in as-tempered conditions. Based on this and previous results on 9 to 12 pct Cr steels, a new equation for the Cr equivalent is proposed and correlated with the amount of δ -ferrite formation. Results indicate that the new Cr equivalent equation shows better correlation than previous equations and predicts the amount of δ -ferrite formed reasonably well.

I. INTRODUCTION

In order to improve the thermal efficiency of fossil power plants, there is a drive to develop high Cr (usually 9 to 12 pct Cr) ferritic steels with excellent creep properties as well as superior oxidation and corrosion resistance properties to those of conventional 1CrMoV, 2.25Cr1Mo, or existing 9 to 12 pct Cr steels. In alloy designing so-called advanced 9 to 12 pct Cr steels, it is very important to estimate the amount of δ -ferrite imbedded in tempered martensite microstructure, because δ -ferrite is known to reduce the notch toughness catastrophically and should be avoided in turbine steels. Effects of alloying elements on the formation of the δ -ferrite are basically related to the role of these elements in expanding or constricting the austenite field. Strong carbide forming elements, such as Ti, V, Mo, W, and Nb, and noncarbide forming elements, such as Si, which are known to constrict the γ field, are expected to increase the δ -ferrite formation, while austenite stabilizing elements, such as Ni, Mn, Co, Cu, C, and N, are expected to play the opposite role.

In an attempt to predict the formation of δ -ferrite in high Cr alloy steels, the concept of Cr equivalent (in wt pct) was introduced, which strictly corresponds to the equivalent amount of Cr in the Fe-Cr binary system that would form the same amount of δ -ferrite at the same temperature. In that context, various equations for the Cr equivalent (Cr_{eq}) are proposed by Thielemann,^[1] Newhouse *et al.*,^[2] Schneider,^[5] Pickering,^[6] and other researchers as well,^[7-14] which are summarized in Table I. All these equations express the Cr equivalent as linear equations of various alloying elements through the regression analysis. Here, coefficients ahead of each alloying element are potency factors normalized to the same amount of Cr in their ability to expand or constrict the γ field, which is related to the δ -ferrite formation. Here, the net Cr equivalent equation by Schneider is deduced by the Schaeffler diagram modified by Schneider showing the effects of Ni and Cr equivalents on the constitutional diagram of stainless steel. In the diagram,

it was shown that the δ -ferrite exists when Cr_{eq} - 0.691 $Ni_{eq} > 10$ pct, where formulas of the Cr and Ni equivalents are given in References 5 and 6. Existing equations differ substantially among themselves and do not predict the formation of δ -ferrite accurately in many cases, which can be ascribed to a different number of alloying elements being included and to the exclusion of higher order and interaction terms among alloying elements.

In the present analysis, several new 9 to 12 pct Cr steels were prepared and the amount of δ -ferrite formed was measured in the as-tempered condition, and a new equation for the Cr equivalent is proposed based on the present and past results.[15–30]

II. EXPERIMENTAL PROCEDURE

Chemical compositions of heats produced in this study are given in Table II. Ingots, 50 kg each, were produced by vacuum induction melting under 10^{-1} to 10^{-3} torr, and subsequently forged at 950 \degree C to 1200 \degree C to bars with 45 \times 100-mm cross section. Forged bars were austenitized at 1100 °C for 4 hours, controlled cooled to room temperature with a cooling rate of 110 $^{\circ}$ C per hour, and subsequently tempered at 700 \degree C for 10 hours before furnace cooling. As-tempered microstructures were examined on surfaces normal and parallel to the forging direction using Vilella's reagent,^[31] and the area fractions of δ -ferrite were measured using the image analyzer. Usually 20 measurements, each covering an area of 1.0×0.75 mm, were made out of a specimen, from which an average was taken.

III. RESULTS AND DISCUSSIONS

The amount of δ -ferrite in as-tempered heats is shown in Table III, and typical optical micrographs with varying amounts of δ -ferrite are shown in Figure 1. Note that the ^d-ferrite formation preferentially takes place along grain boundaries or grain boundary triple junctions. Based on the ^d-ferrite measurements of the 29 heats mentioned earlier and previous reports, $[15-30]$ a new equation for the Cr equivalent is proposed here as follows:

$$
Cr_{eq} (pot) = Cr + 0.8Si + 2Mo + 1W + 4V + 2Nb + 1.7Al + 60B + 2Ti + 1Ta [1] - 2.0Ni - 0.4Mn - 0.6Co - 0.6Cu - 20N - 20C
$$

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Table I. Proposed Equations for the Cr Equivalent and the Criteria to Avoid the δ -Ferrite Formation in 9 to 12 Pct Cr Steels

Equations	Criteria for No δ -Ferrite	References
1. Cr_{eq} (pct) = Cr + 5.2Si + 4.2Mo + 2.1W + 11V + 4.5Nb + 12Al + 7.2Ti $-3Ni - 2Mn - 40N - 40C$		
2. Cr_{eq} (pct) = Cr + 1.5Si + 2V + 3Nb + 2.5Al + 7.2Ti + 10Zr - 3Ni - 2Mn $-2Cu - 40N - 40C$		
3. Cr_{eq} (pct) = Cr + 6Si + 4Mo + 1.5W + 11V + 5Nb + 12A1 + 8Ti + 2.5Ta $-4Ni - 2Co - 2Mn - 1Cu - 30N - 40C$	Cr_{eq} < 10 pct	2, 3, 4
4. net Cr_{eq} (pct) = $Cr + 2Si + 1.5Mo + 0.75W + 5V + 1.75Nb + 5.5Al + 1.5Ti$ $-0.691(Ni + Co + 0.5Mn + 0.3Cu + 25N + 30C)$	net Cr_{eq} < 10 pct	5, 6
5. Cr_{eq} (pct) = Cr + Si + 2Mo + 1.5W + 4V - 2.3Ni - 0.3Mn	Cr_{eq} < 15 pct	8
6. Cr_{eq} (pct) = $Cr + 2Si + 1.5Mo - 2Ni - Mn - 15N$	$Cr_{eq} - 7.5C < 8.2$ pct	9, 10
7. *Md = $1.059Cr + 1.034Si + 1.663Mo + 1.836W + 1.610V + 2.335Nb + 2.486Ta$ $+ 2.497$ Ti + 0.755Co + 0.637Cu + 0.825Fe - 0.4N - 0.23C	Md < 0.852	11
8. δ -ferrite (pct) = 14Cr + 6Si + 5Mo + 18V + 54Al - 220N - 210C - 20Ni $-7Co - 7Cu - 6Mn$		12
9. δ -ferrite (pct) = 12.1Cr + 32.9Si + 39.1Mo + 46.1V + 83.5Nb - 555C - 476N $-49.5Mn - 28.7Ni - 697B - 104$		13
10. δ -ferrite (pct) = 2.962 + 1.885 (heat input per unit length, kJ/mm)		14
11. Cr_{eq} (pct) = Cr + 0.8Si + 2Mo + 1W + 4V + 2Nb + 1.7Al + 60B + 2Ti + 1Ta -2.0 Ni -0.4 Mn $-0.6C_0 - 0.6C_u - 20N - 20C$	Cr_{eq} < 10 pct	this study
*Alloying elements in atomic fraction.		

Table II. Chemical Compositions of the Alloys (Weight Percent)

Other elements: 0.010 to 0.020 pct P; 0.006 to 0.010 pct S.

Table III. Cr Equivalent and δ-Ferrite Contents of the **Alloys Studied in the Present Analysis (Weight Percent)**

Alloy	Cr_{eq} *	** Cr_{eq}	$\operatorname{Cr}_{eq}{}^{\dagger}$	δ -Ferrite [‡]	
Number	(Wt Pct)	(Wt Pct)	(Wt Pct)	(Pct)	Std^s
BC1	12.09	13.19	12.74	41.1	3.24
BC2	9.04	11.38	10.84	12.5	1.59
BC ₃	7.16	10.41	9.91	$\mathbf{0}$	$\mathbf{0}$
BC4	4.79	9.18	8.72	$\overline{0}$	$\mathbf{0}$
W35B1	10.42	12.25	11.62	11.4	1.10
W35B2	10.41	12.28	12.06	16.5	2.67
CW30B1	8.11	10.86	10.35	0.2	0.08
CW30B2	7.71	10.66	10.50	0.8	0.40
BW10	2.5	7.11	6.28	$\mathbf{0}$	$\mathbf{0}$
BW25	6.63	9.60	9.12	$\mathbf{0}$	$\mathbf{0}$
BW35	7.55	9.81	9.38	0.1	0.01
BW55	10.88	11.72	11.55	2.5	0.66
BW20Cr1	5.45	9.39	8.46	$\mathbf{0}$	$\mathbf{0}$
BW30Cr1	8.08	10.79	10.39	2.3	0.39
BW20Cr2	7.08	10.63	9.96	θ	$\mathbf{0}$
CoC1	8.54	10.67	11.20	10.7	2.93
CoC2	7.04	9.89	10.47	1.7	0.39
CoC3	5.50	9.15	9.76	$\mathbf{0}$	$\overline{0}$
CoC3Mo	7.28	9.86	10.71	0.6	0.24
CoC3Cr	5.37	9.37	9.94	$\mathbf{0}$	$\mathbf{0}$
CoW35B1	7.08	10.38	10.74	0.8	0.41
CoW25B2	4.11	8.99	9.35	$\mathbf{0}$	$\overline{0}$
CoW35B2	6.94	10.32	11.01	1.4	0.68
Cu10	8.83	10.35	9.99	$\mathbf{0}$	$\mathbf{0}$
Cu20	6.48	10.08	9.21	$\mathbf{0}$	$\mathbf{0}$
Cu ₂₀ Mo	8.66	10.84	10.11	< 0.1	$\boldsymbol{0}$
Cu ₂₀ Cr	5.51	10.18	9.03	$\mathbf{0}$	$\overline{0}$
CuW35B2	9.51	11.43	10.28	< 0.1	$\boldsymbol{0}$
CuCoW35B2	6.96	9.94	9.54	$\mathbf{0}$	$\mathbf{0}$

*,**,†Calculated values of Cr equivalent using the proposed equations by Newhouse et al.,^[2] Schneider,^[5] and the present analysis, respectively. τ The amount of δ -ferrite measured in the present work.

§ Corresponding standard deviations.

Here, all chemical compositions are in weight percent, and the potency factors, numerical coefficients ahead of each alloying element, were deduced by multiple regression. The regression analysis included only the major alloying elements, such as Cr, W, C, and Ni initially, but extended to cover remaining elements subsequently.

This equation differs from that of Thielemann,[1] which is based on the Fe-based system, and also from that of Newhouse *et al.*,^[2] which modified the Thielemann equation to 9 to 12 pct Cr steels. The Newhouse equation shows that the δ -ferrite does not form for Cr_{ea} < 10 pct. Compared to the Newhouse equation, potency factors of carbide forming elements (or δ formers), such as Mo, V, Ti, and W, plus Si and Al are substantially lower, and even those of γ formers, such as Ni, Mn, Co, and Cu, are mildly lower in the present study. Potency factors of the present study are pretty much similar to those of Schneider,[5] except Si (lowered), Al (lowered), Ni (increased), and B that is newly added. In advanced 9 to 12 pct Cr steels, boron is added to 150 ppm to increase the creep rupture strength $[22]$ and known to reduce the amount of δ -ferrite.^[13] However, the present study reveals that B enhances the δ -ferrite formations contrary to the previous reports (*cf*. compare alloys W35B1 to W35B2, CW30B1 to CW30B2, and CoW35B1

to CoW35B2). Generally, B is a γ constricting element, and formation of borocarbide can expedite the δ -ferrite formation by reducing the amount of C dissolved in the matrix.

The Newhouse criterion does not predict δ -ferrite formation for Cr_{eq} < 10 pct; nonetheless, results of BW30Cr1 and CoC1 alloys shown in Figure 1 show the presence of d-ferrite, presumably due to the overestimated potency factors of Ni, Mn, and Co. On the other hand, the Schneider equation predicts the formation of δ -ferrite for net Cr_{eq} > 10 pct, for BC3, BW20Cr2, Cu10, and Cu20Cr alloys, which was not verified experimentally here (for the definition of net Cr*eq*, refer to Eq. [4] in Table I). Thus, the roles of Ni and Cu appear to be underestimated in the Schneider equation.

In Figure 2, amounts of δ -ferrite found in tempered alloy steels are plotted as functions of several Cr equivalents, namely, Newhouse, Schneider, and the present equation. Data are from 228 alloys presented in the present work and previous reports.[15–30] It can be seen that the scattering band improves in the order of Newhouse, Schneider, and the present work. Large scatters were found in $W > 1.5$ pct and $Ni > 1$ pct in the Newhouse equation. The figure also demonstrates that the Schneider equation shows a substantial improvement over Newhouse's and that the present equation can be used in a wide range of 9 to 12 pct Cr alloy steels.

In alloy designing high Cr alloy steels for turbine rotors, it is important to know the optimum amount of each alloying element that does not form δ -ferrite. Being a measure to form ^d-ferrite, the Cr equivalent provides a useful criterion. For example, the criteria to form δ -ferrite are $Cr_{eq} > 10$ pct and net Cr_{eq} > 10 pct for the Newhouse and Schneider equations, respectively. Strictly speaking, these critical values should coincide with the Cr content of the $\gamma/\gamma + \delta$ boundary in the Fe-Cr-C phase diagram[32] at a fixed C content when all other alloying elements are absent, which is $Cr = 13.23$ pct at 0.1 pct C. The Newhouse equation gives $Cr = 14$ pct, which is reasonably close to that of the phase diagram, while the Schneider equation gives $Cr = 12.07$ pct. From Figure 2(c), it can be seen that δ -ferrite starts to form at Cr_{eq} = 11.0 \pm 1.0 pct in the present work. Taking the lower limit, we take $Cr_{eq} = 10$ pct as a conservative criterion to be kept to avoid the δ -ferrite formation. This corresponds to Cr = 12.0 pct at 0.1 pct C in the Fe-Cr-C ternary system, which is 1.23 pct lower than that of the phase diagram. The difference can also be interpreted as a safety margin, which takes account of δ ferrite formation under nonequilibrium conditions such as segregation of ferrite forming elements during the solidification process.

In some cases, such as in boiler tube steels or dual phase steels, the presence of a small amount of δ -ferrite is beneficial to good weldability and formability, and a method to predict the amount of δ -ferrite present is desired. Here, we propose a relation between δ -ferrite content (Y, in vol pct) and the Cr equivalent $(X, \text{ in wt})$ at 1100 °C based on our regression analysis, as follows:

$$
Y = 340.43 - 71.75 X + 3.77 X2, 10 \text{ pct} \le X \le 12 \text{ pct}
$$

$$
Y = -146.32 + 13.94 X, \qquad X > 12 \text{ pct}
$$
 [2]

The accuracy of the proposed equation can be seen from the high sample correlation coefficients (above 0.92) as well as from Figure 3, which shows the correlation between the calculated and measured amounts of δ -ferrite. The two

Fig. 1—Optical micrographs of as-tempered microstructures of (*a*) W35B2 (δ = 18.5 pct), (*b*) BW25 (δ = 0 pct), (*c*) BW30Crl (δ = 2.3 pct), (*d*) CoCl $(\delta = 10.7 \text{ pct})$, (*e*) CoC3Mo ($\delta = 0.6 \text{ pct}$), and (*f*) CuW35B2 ($\delta = 0.1 \text{ pct}$).

showed the scattering band of only 16 pct, which may come from varying austenitization temperatures, macro- and microsegregation, etc. According to Eq. [2], it can be seen that 100 pct δ -ferrite forms when $Cr_{eq} = 17.67$ pct.

IV. CONCLUSIONS

1. A new equation for the Cr equivalent is proposed for 9 to 12 pct Cr steels, as follows:

$$
Cr_{eq} (pot) = Cr + 0.8Si + 2Mo + 1W + 4V + 2Nb + 1.7Al + 60B + 2Ti + 1Ta - 2.0Ni - 0.4Mn - 0.6Co - 0.6Cu - 20N - 20C
$$

The equation takes into account the effect of B, Ni, and Co reasonably well.

Fig. 2—Correlations between experimentally measured amount of δ -ferrite and proposed Cr equivalent equations by (*a*) Newhouse *et al.*,^[2] (*b*) Schneider,^[5] and (*c*) the present work.

Fig. 3—Correlations between the measured and calculated amounts of δ ferrite.

- 2. A conservative rule to be kept to avoid the δ -ferrite formation in this type of steel is proposed as Cr_{eq} < 10 pct.
- 3. For $\text{Cr}_{eq} \geq 10$ pct, the amount of δ -ferrite (Y) is related to the Cr_{eq} (X), as follows, within the accuracy of \pm 8 pct:

 $Y = 340.43 - 71.75 X + 3.77 X^2$, 10 pct $\le X \le 12$ pct

 $Y = -146.32 + 13.94 X$, $X > 12$ pct

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