Title

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Authors

Kung, C.Y.
Rayment, J.J.

Publication Date

1981-08-01

LBL-13191
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to Metallurgical Transactions

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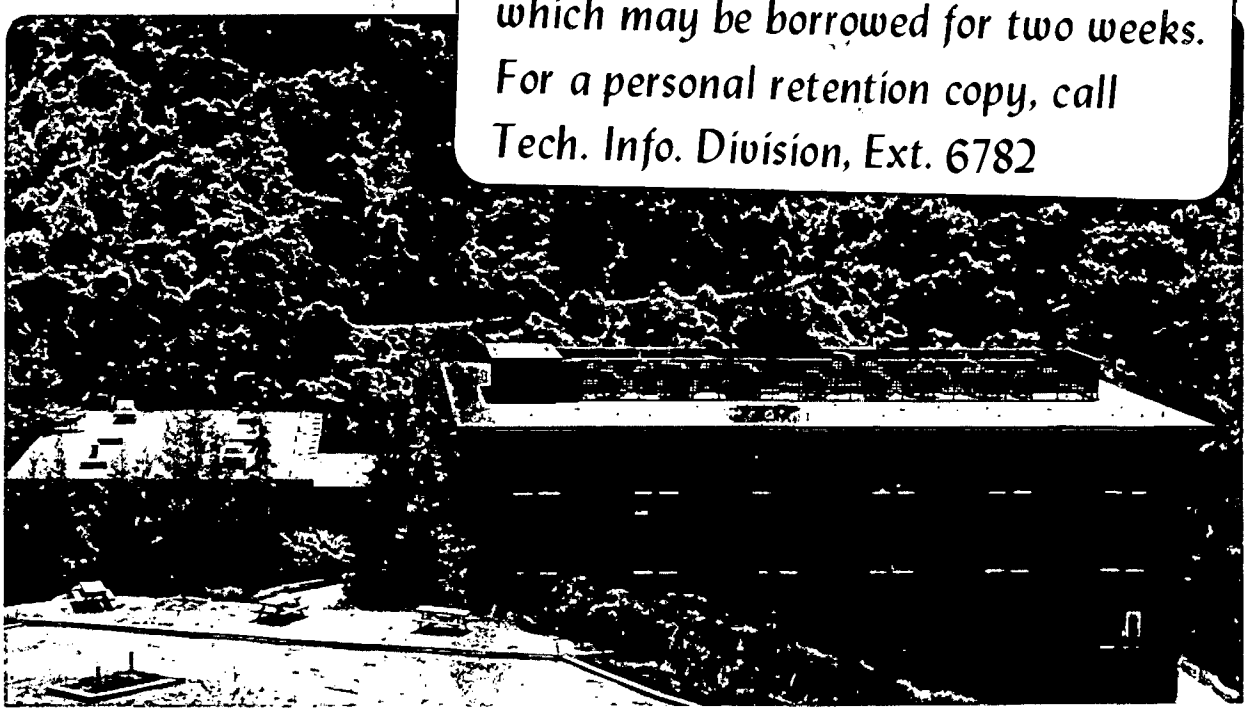
C.Y. Kung and J.J. Rayment

August 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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An Examination of The Validity of Existing Empirical Formulae For The Calculation of M_s Temperature.

by

C.Y.Kung and J.J.Rayment

Staff Scientists, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California, 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

AN EXAMINATION OF THE VALIDITY OF EXISTING EMPIRICAL FORMULAE FOR THE CALCULATION OF M_s TEMPERATURE

C. Y. Kung and J. J. Rayment

When examining phase transformations in ferrous systems, it is often desirable to have prior knowledge of the martensite **start** temperature (M_s). In the area of martensitic transformations, there has been considerable debate about the factors responsible for promoting twinning in the martensite structure. It has been suggested that M_s plays an important role--lowering the M_s results in an increase in the probability of internal twinning.[1-3] The M_s temperature has also been shown to have a direct effect on the toughness of steels. Quenched steels which have a high M_s are usually dislocated packet martensites and also have been shown to undergo significant autotempering,[4] both factors being beneficial to toughness.

On a more basic level, a knowledge of the M_s temperature can be useful, to ensure that a heat treatment and subsequent kinetic study of bainitic transformations occurs in a temperature range above the M_s temperature.

It is well known that the M_s temperature is strongly dependent on the composition of the parent phase, austenite. Izumiyama et al.[5] have shown the effect of individual alloying elements upon the M_s temperature for iron-based binary alloys. Their results show that Al, Ti, V and Co effectively increase the M_s temperature, whereas Nb, Cu, Cr, Mo, Ni, C, and N decrease the M_s temperature. There have been several formulae which have attempted to relate the M_s temperature with alloy composition, (with the assumption that all alloying elements

including carbon are in complete solution). These formulae are shown in Table I,[6-12] with minor modifications shown in parentheses which are described later. In these formulae, cobalt is the only element included which slightly increases the M_s temperature, a result confirmed by several recent investigations.[13-14] Moreover, cobalt is included only in one formula, that of Carapella. The coefficient for cobalt is rather high, compared to that for nickel or chromium. But the results of Izumiyama et al., Figure 1, show that the slope for cobalt is only about 10° per atomic percent, i.e. about 10° per weight percent. In some low alloy carbon steels[13,22,32] the addition of Co does show an increase of M_s by about 8°C to 12°C per percent increase. Therefore, in the present investigation, all equations except Carapella's equation have been modified to take this into account. The effect of silicon on the M_s temperature is uncertain. In some cases, silicon has been found to raise the M_s,[15] but in the formulae of Rayson and Savage, Carapella, Rowland and Lyle, and Nehrenberg, the coefficient for silicon is shown to be negative. For this investigation, the effect of silicon is considered to be equivalent to that of molybdenum.. Therefore, a term of -7.5 Si has been included in some of the equations.

To date, the most complete analysis of M_s temperature as a function of composition has been described by Andrews et al. in 1965. He developed both linear and product formulae for the M_s temperature based on a total of 184 carefully selected sets of experimental M_s temperatures and corresponding chemical analyses of steels. The maximum alloying content used in this analysis were 0.6% C, 4.9% Mn, 5% Cr, 5% Ni and 5.4% Mo. Recently Krauss[16] has tested the Andrews linear relationship with an additional fifty measured M_s-composition data sets and found a reasonable agreement between measured and

calculated M_s temperatures. Another investigation recently carried out, examined the existing formulae using the measured M_s - composition data for 21 low alloy steels. Llopis[17] found that the formulae developed by Nehrenberg gave the best fit for the experimental results, followed by Payson and Savage, Rowland and Lyle, and Andrews (non-linear). However, the conclusions obtained are a little crude, and the range of alloy composition and data collected rather limited.

The aim of the present investigation is to test the existing M_s formulae with the measured M_s - composition data collected over the past 15 years in the alloy design programs at Berkeley. In the past decade, these systematic studies of martensitic steels have provided extensive data of measured M_s temperatures for a large range of compositions. The maximum total composition of alloying elements in the steels studied is about 21 wt percent, and the maximum individual elemental compositions are 0.5% C, 12.2% Cr, 2.1% Mn, 12.5% Ni, 4.2% Mo, 3.2% Si and 9% Co. These values are beyond the composition limit allowed by the existing M_s formulae. However, this investigation involves examining the validity of existing formulae in predicting M_s temperatures in the high alloy range as well as in the low alloy range.

The M_s temperatures for the steels studied at Berkeley have been measured by means of a commercial dilatometer (Thelta Dilatronic III R dilatometer), with quenching rates in the range 50-135°C per second. In this regime, it has been shown previously that the rate of quenching has little effect on the M_s temperature.[14] The austenitizing temperatures used ranged from 870-1200°C. Previous studies have shown that the M_s temperature varies by about 25°C in this austenitizing range.[18-21] The austenitizing time has also been shown to have a

slight effect on the M_s.[20] Therefore, it is reasonable to assume a likely error of about 25°C in the subsequent calculations due to these experimental factors. Thus, if a calculated M_s temperature falls within 25°C of the measured, value, it shows a good fit.

Table II shows the percentage of calculated data which falls within the limit of 25°C. H in the table denotes high alloy steels (>7 wt% alloying element) and L denotes low alloy steels. The results show that all the formulae with the exception of Grange and Stewarts', are fairly good at estimating M_s temperatures for low alloy steels. For more than 80% of low alloy steels, the M_s temperature can be predicted by these formulae within $\pm$ 25°C. However, when predicting the M_s temperature for high alloy steels, only Andrews' linear equation and Steven and Haynes' equation give reasonable fits. The standard deviation ($\overline{|\Delta M_s|}$) for Andrews, and Steven and Haynes' equations are only 13.4° and 17° respectively.

In examining the M_s formulae, it becomes necessary to explore the possible errors involved in some of the equations. In the determination of M_s for high alloy steels, Carapella's product-type equation has been found to be the least accurate. The error here probably arises from the improper mathematical form (i.e. the product form), that is chosen to describe the interaction effect of two or more alloying elements. When Carapella's formula is expanded into a non-linear additive form, the coefficient on each second order term (except the term involving cobalt) becomes positive which makes the interaction of the two elements have a positive effect on the M_s temperature. Such a positive effect is not easily explained. The formulae of Payson and Savage, Rowland and Lyle, Grange and Stewart, and Nehrenberg did not fit the measured data very well, particularly for data

points for steels containing a high percentage of chromium. The discrepancy between measured and calculated M_s for the Andrews' nonlinear equation is also due to the effect of chromium. The chromium coefficient (15 - 67.6C) becomes positive when the carbon content is less than 0.22%. This effect produces a large deviation from the measured value for high chromium--low carbon alloys (see Figure 2a).

The good fits obtained for Andrews' linear, and Steven and Haynes' equation are shown in Figures 2b and 2c respectively. Although both show small deviation from the measured M_s temperatures (the former shows a deviation for high chromium alloys, the latter for high molybdenum alloys), nevertheless, the two formulae are reasonably good in estimating the M_s temperature for both low and high alloy steels.

In this study we have modified the existing M_s temperature equation by considering also the effects of cobalt and silicon. The modified Andrews' linear equation, and Steven and Haynes' equation have been shown to be reasonably good in estimating the M_s temperature for both low and high alloy steels. However, the Andrews' linear equation has slightly overestimated the case for high chromium alloys whereas Steven and Haynes' equation on the other hand, underestimated the case for high molybdenum alloys. Appropriate modifications and care must be taken in the application of either equation.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U. S. Department of Energy, under Contract No. W-7405-ENG-48. Both authors wish to acknowledge the advice of Professor G. Thomas.

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Table I. List of Formulae for M_s Calculation

References	
Payson and Savage (6)	$M_s(°C) = 499 - 308C - 32.4Mn - 27Cr - 16.2Ni - 10.8Si - 10.8Mo - 10.8W + (10Co)$
Carapella (7)	$M_s(°C) = 496 \times (1 - 0.62C)(1 - 0.092Mn)(1 - 0.033Si)(1 - 0.045Ni)(1 - 0.07Cr)(1 - 0.029Mo)(1 - 0.018W)(1 + 0, 0.12Co)$
Rowland and Lyle (8)	$M_s(°C) = 499 - 324C - 32.4Mn - 27Cr - 16.2Ni - 10.8Si - 10.8Mo - 10.8W + (10Co)$
Grange and Stewart (9)	$M_s(°C) = 538 - 350C - 37.7Mn - 37.7Cr - 18.9Ni - 27Mo + (10Co)$
Nehrenberg (10)	$M_s(°C) = 499 - 292C - 32.4Mn - 22Cr - 16.2Ni - 10.8Si - 10.8Mo + (10Co)$
Steven and Haynes (11)	$M_s(°C) = 561 - 474C - 33Mn - 17Cr - 17Ni - 21Mo + (10Co - 7.5Si)$
Andrews (12)	$M_s(°C) = 539 - 423C - 30.4Mn - 12.1Cr - 17.7Ni - 7.5Mo + (10Co - 7.5Si)$
Andrews (12)	$M_s(°C) = 512 - 453C - 16.9Ni - 9.5Mo + 217(C)^2 - 71.5(C)(Mn) + 15Cr - 67.6(C)(Cr) + (10Co - 7.5Si)$

Table II. Summary of Analysis of Data for Existing M_s Formulae

	A(%)	B(%)	$\Delta\overline{M}_s$	$\lvert\overline{\Delta M_s}\rvert$
Payson & Savage	H 26.7 L 82.0	58	-24	30
Carapella	H 20.0 L 74.4	51	-14.6	41.6
Rowland & Lyle	H 17.7 L 82.0	58	-27.3	32.6
Grange & Stewart	H 33.3 L 82.0	46	-24.8	44.3
Nehrenberg	H 53.3 L 84.6	71	-11.5	21.9
Steven & Haynes	H 80 L 84.6	83	- 4.5	17
Andrew (linear)	H 83.3 L 94.9	90	3.8	13.4
Andrew (non-linear)	H 66.7 L 89.8	80	5.9	19.7

A and B are of calculated data within a limit of 25°C of experimental data. A denotes the values for high alloys and low alloys; B denotes the values for all alloys. $\Delta\overline{M}_s$ is the mean deviation, $\lvert\overline{\Delta M_s}\rvert$ is the standard deviation.

Figure Captions

Fig. 1. M_s temperature of Fe-base binary alloys (after Izumiyama *et al.*[5]).

Fig. 2. Comparison of experimental M_s measurement and M_s calculated from composition according to (a) Andrews' nonlinear equation, (b) Andrews' linear equation, and (c) Steven and Haynes' equation.

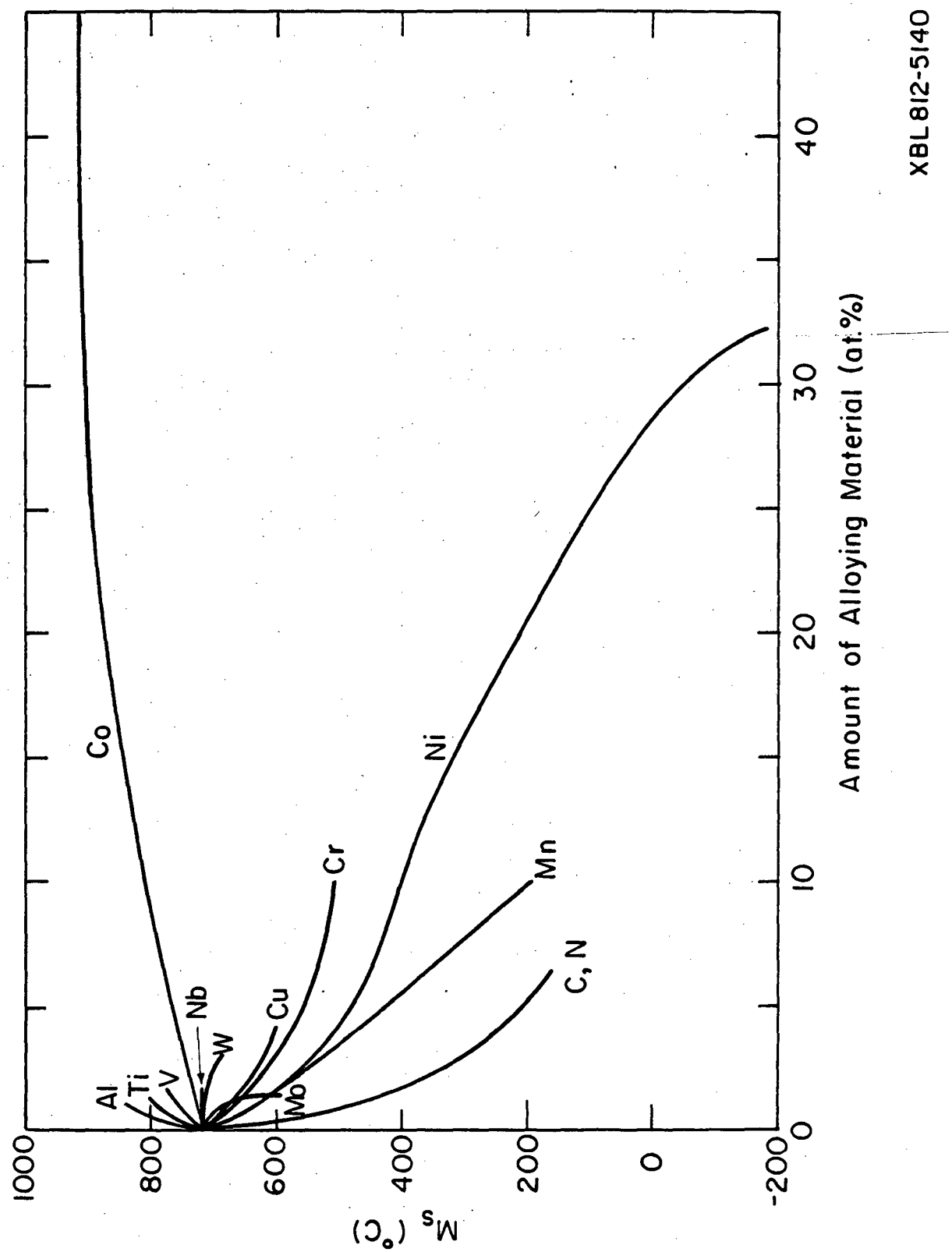
XBL812-5140
Amount of Alloying Material (at.%)
M_s (°C)
1000
800
600
400
200
0
-200
0
10
20
30
40
Co
Ni
Cr
Mn
C, N
Cu
Nb
W
Mo
V
Ti
Al

Fig. 1

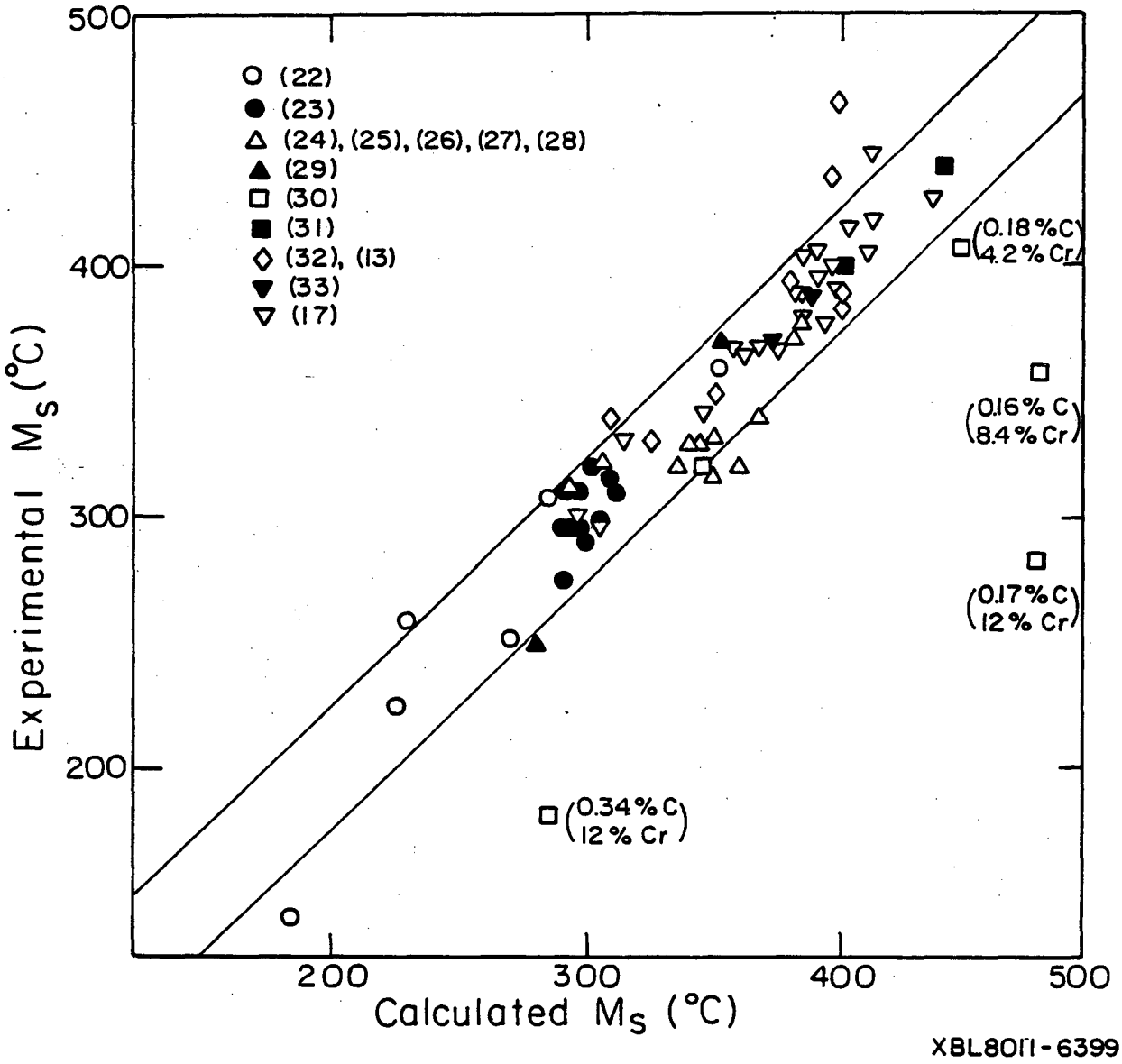
500
400
300
200
200
300
400
500
Experimental M_S (°C)
Calculated M_S (°C)
○ (22)
● (23)
△ (24), (25), (26), (27), (28)
▲ (29)
□ (30)
■ (31)
◇ (32), (13)
▼ (33)
▽ (17)
(0.18 %C 4.2 % Cr)
(0.16 % C 8.4 % Cr)
(0.17 % C 12 % Cr)
(0.34 % C 12 % Cr)
XBL8011-6399

Fig. 2a

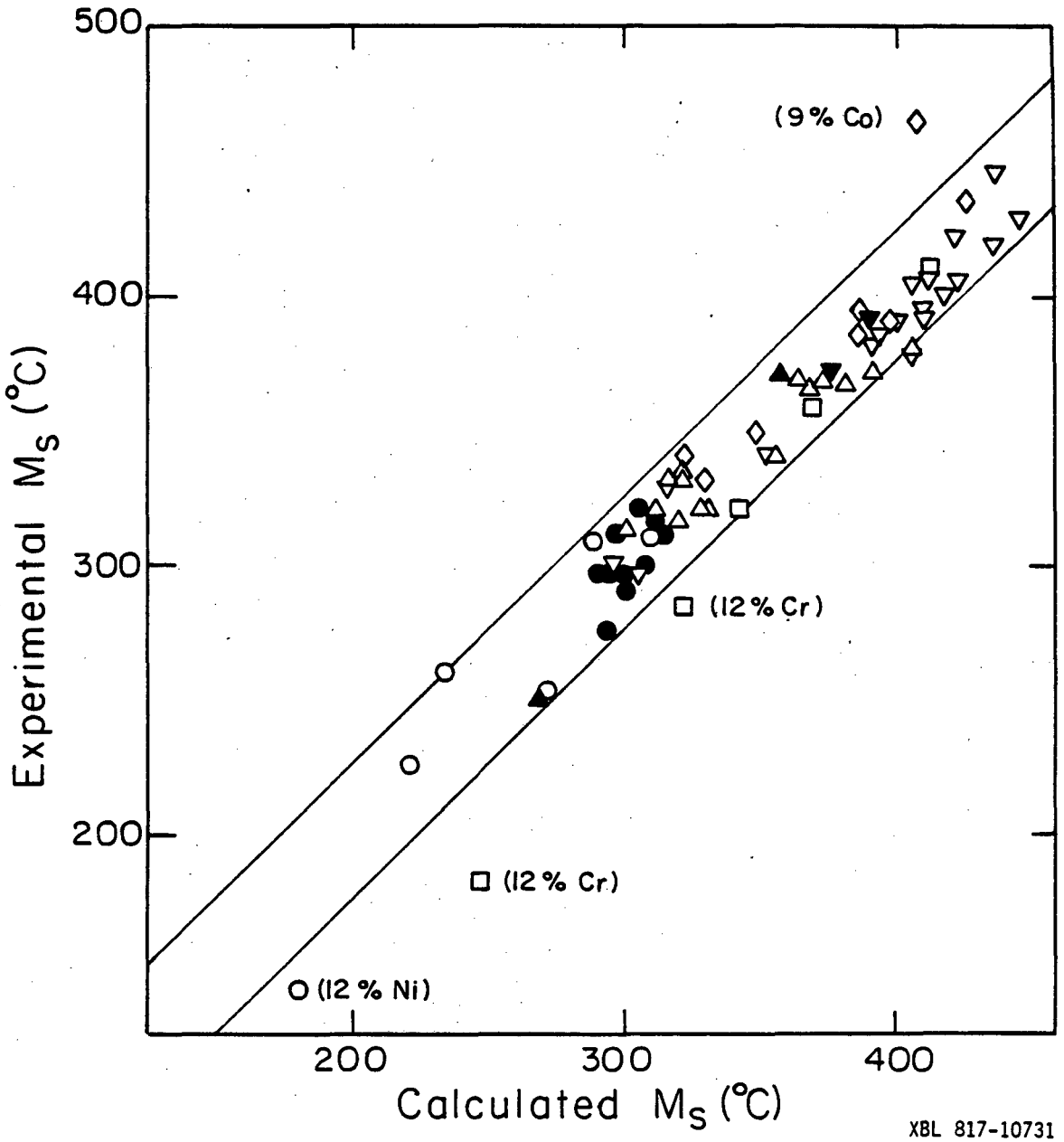
500
400
300
200
Experimental M_S (°C)
(9% Co)
(12% Cr)
(12% Cr)
O (12% Ni)
200
300
400
Calculated M_S (°C)
XBL 817-10731

Fig. 2b

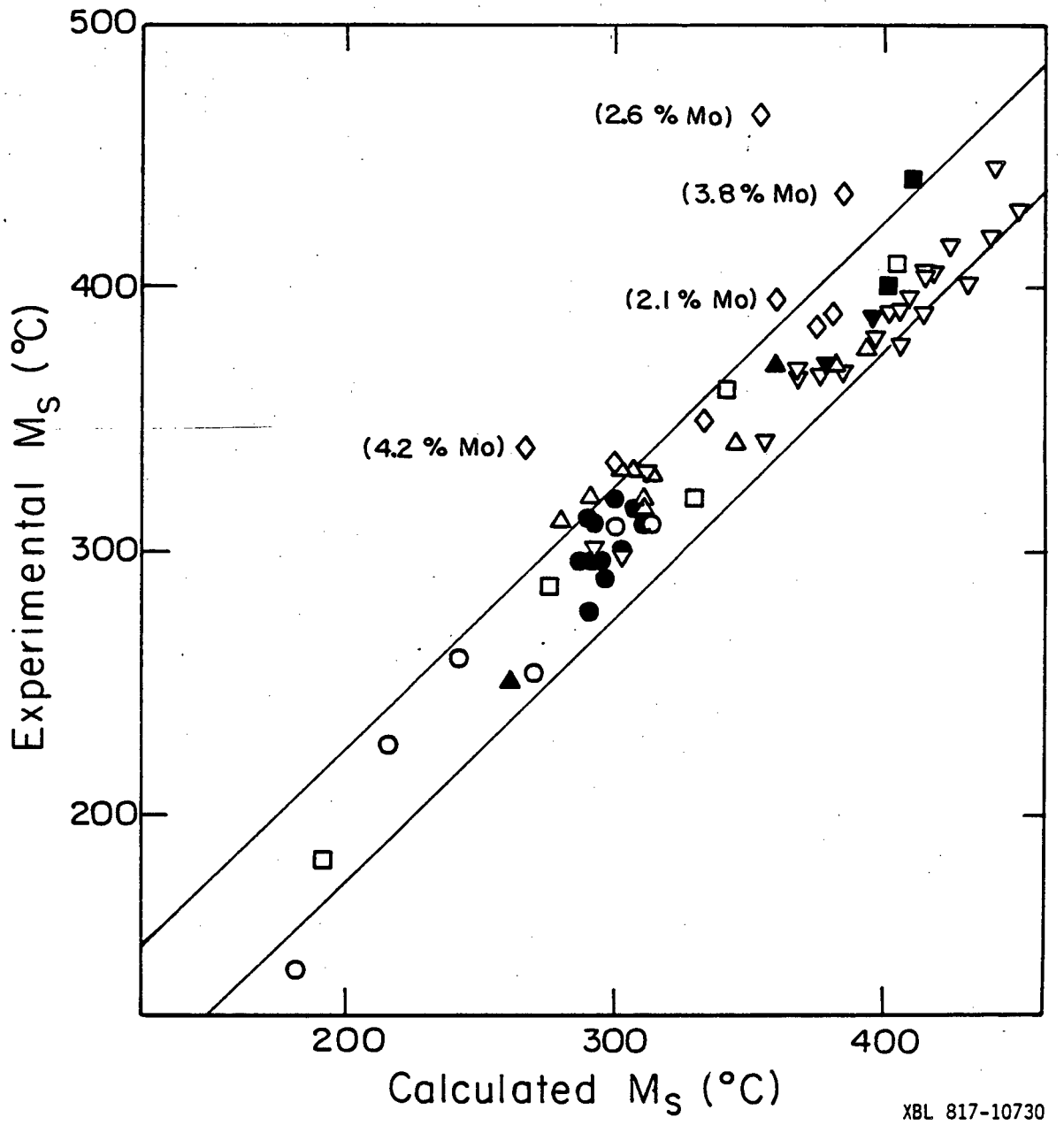
500
400
300
200
200
300
400
Experimental M_S (°C)
Calculated M_S (°C)
(2.6 % Mo)
(3.8 % Mo)
(2.1 % Mo)
(4.2 % Mo)
XBL 817-10730

Fig. 2c

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