X-641-65-265

NASA TM X-55268

[redacted]

THE FORMATION OF THE KAMACITE PHASE IN METALLIC METEORITES

GPO PRICE $ ______

CSFTI PRICE(S) $ ______

Hard copy (HC) 2.00

Microfiche (MF) .50

ff 653 July 65

BY

J. I. GOLDSTEIN

FACILITY FORM 602

N65-33750	
(ACCESSION NUMBER)	(THRU)
28	1
(PAGES)	(CODE)
TMX-55268	06
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

JUNE 1965

NASA

GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

X-641-65-205

THE FORMATION OF THE KAMACITE PHASE IN METALLIC METEORITES

by
J. I. Goldstein

JUNE 1965

The Formation of the Kamacite Phase in Metallic Meteorites

J. I. Goldstein
National Aeronautics and
Space Administration
Greenbelt, Maryland

June 7, 1965

The Formation of the Kamacite Phase in Metallic Meteorites

J. I. Goldstein
National Aeronautics and
Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

33750

Abstract. In order to predict the concentration gradients in meteoritic kamacite, the newly determined Fe-Ni phase diagram of Goldstein and Ogilvie was applied and a diffusion analysis was developed. The results of the diffusion analysis show that the kamacite phase cannot remain in equilibrium at low cooling temperatures and a Ni depletion in the kamacite near the α/γ interface occurs below 450°C. In addition certain other features of the kamacite phase are predicted: (1) An increasing Ni concentration from the center of the kamacite phase towards the α/γ interface in coarse and medium octahedrites, (2) A variation in the average Ni content of the average sized kamacite bands with the overall Ni content of the meteorite, and (3) The average composition of kamacite plates of the same width is the same no matter what the overall Ni content of the parent meteorite is.

These predictions have been confirmed by electron probe measurements of several metallic meteorites. This correlation is in agreement with cooling rates of parent bodies which form at low pressures. author

Introduction. The formation of the Widmanstatten pattern in metallic meteorites has recently been discussed by Goldstein and Ogilvie [1965a] and by Wood [1964]. The results of these studies showed that the iron meteorites formed under conditions of low pressure and in parent bodies which cooled at a rate of about $1\text{-}10^{\circ}/10^{6}$ years. Therefore the one atmosphere Fe-Ni phase diagram can be used to describe phase equilibria in iron meteorites and the one atmosphere diffusion coefficients can be used to describe the mass transport of material through the kamacite and taenite phases in iron meteorites. It is the purpose of this paper to predict the composition variations that would occur in the kamacite phase of metallic meteorites if they had cooled at an average rate of about $2^{\circ}/10^{6}$ years at low pressures. A comparison will then be made between predicted composition variations and measured data.

The Fe-Ni Phase Diagram. The one atmosphere Fe-Ni phase diagram has been recently redetermined by Goldstein and Ogilvie [1965b], Figure 1. The Ni solubility in α and γ phase was determined experimentally from 800°C to 500°C and calculated theoretically below this temperature. The maximum Ni solubility in kamacite was calculated to occur at about 450°C. The diagram differs from Owen and Liu's [1949] in that the range of Ni solubility in the alpha phase is larger above 500°C and that the Ni solubility in α bends back to lower Ni contents above 300°C.

Theory. Small concentration gradients have been measured in the kamacite phase of iron meteorites [Agrell, Long, and Ogilvie, 1963]. This indicates that at some time during the cooling of the meteorite, equilibrium conditions were no longer maintained in the kamacite phase. In other words, at some temperature during cooling the composition of the kamacite could not be maintained at the value given by the phase diagram. This nonequilibrium behavior occurs because not enough Fe and Ni can be transferred across the kamacite phase (i.e. low diffusion rates) to maintain equilibrium within the time available.

In order to describe this process in more detail a calculation was made of the largest sized kamacite plate of half width W that could remain homogeneous at a temperature T_o. In this study, the half width of the kamacite phase is measured across the phase, perpendicular to the α/γ interface. A certain number of assumptions are made in this calculation: (1) The parent body cools at a rate of $2^o/10^6$ years; (2) The process of homogenization is diffusion controlled; (3) The cooling occurs in a stepwise process; and (4) In each interval of cooling Δt, the homogenization process occurs isothermally at an average temperature T_o.

The method of calculation is shown schematically in Figure 2. At time $t = 0$, the kamacite phase is assumed homogeneous at a Ni content C_o given by the equilibrium phase diagram. From time $t = 0$ to $t = \Delta t$, the equilibrium compoisition at the kamacite/taenite interface is assumed equal to C_1. During the time increment Δt, the Ni content of the kamacite phase will increase. For the assumed cooling rate and the temperature T_o, the amount to which C, the Ni content at the center of the kamacite phase, approaches C_1, is determined by the diffusion coefficient of mass transport in kamacite D_α. The maximum width W of kamacite for which the degree of homogenization,

$$\left((C-C_o)/(C_1-C_o)\right)_{\Delta t}$$

is equal to some ratio approaching 1, is that width which can still remain homogeneous at temperature T_o. Since D_α is a function of T_o, one can calculate W as a function of temperature.

The interdiffusion coefficients D_α [Goldstein and Ogilvie, 1965c] as well as the self diffusion coefficients D^*_{Ni} in α iron have been measured [Borg and Lai, 1963]. Good agreement between the interdiffusion measurements [Goldstein and Ogilvie, 1965c] and the self diffusion coefficients of Borg and Lai [1963] has been found. The formation of kamacite occurs below the Curie temperature of pure iron. Unfortunately the activation energy for diffusion has not been measured below this temperature. Using the calculation of excess activation energy ΔH due to the magnetic effect [Borg and Lai, 1963] and the measurement of ΔH above the Curie temperature, the value of D_α is estimated and given by the following equation:

$$D_\alpha = 9.9 \exp (-64{,}300/RT_o) \qquad (1)$$

The degree of homogenization and the time interval Δt used for the calculation are interrelated since the difference (C_1-C_o) depends on the value of Δt. Calculations were made for two different criteria of homogeneity, a difference of .01 and .03 atomic % Ni between the center of kamacite and the α/γ boundary. If a value of Δt is used, corresponding to a time period for $25^\circ C$ of cooling, the degree of homogenization at $600^\circ C$ corresponds to .97 and .90 respectively. Using the relations between W, D_α and

$$\Big((C-C_o)/(C_1-C_o)\Big)_{\Delta t}$$

given by Crank [1956] the maximum width of kamacite which can remain homogeneous is given by $W = \sqrt{D\ \Delta t/1.5}$ and $W = \sqrt{D\ \Delta t}$ for

$$\Big((C-C_o)/(C_1-C_o)\Big)_{\Delta t} = .97 \text{ and } .90$$

respectively. For other compatible values of Δt and the degree of homogenization, one obtains substantially the same answers. Figure 3 shows the results of these calculations.

In any metallic meteorite, there is a distribution of kamacite band widths which usually range from micron to mm size. The distribution of band widths shows a maxima, in a small range of kamacite band sizes (usually the largest sized bands). It is bands of this general size which compose the Widmanstatten pattern in octahedrites. The average of this small range of band sizes is designated as the 'average sized kamacite band width of the meteorite.'

'Average sized kamacite bandwidths' and the overall Ni composition of the meteorite are usually related. As the overall Ni content increases, the size of the average kamacite bands decreases. Table I classifies octahedrites according to the size of the kamacite bands [Lovering, Nichiporuk, Chodos, and Brown, 1956].

TABLE 1

Classification of metallic meteorites

Type	Average Half Width of Kamacite Bands (mm)	Overall Ni Content of Meteorite (wt % Ni)
Coarse Octahedrites (Og)	>1	<7.3
Medium Octahedrites (Om)	.25-1.0	<10.0
Fine Octahedrites (Of)	.025-.25	<16.0
Ataxites, Plessite (A)	<.025	<27.0

According to the results of the calculations, kamacite phases in meteorites which have a typical coarse structure remain homogeneous to about 525°C. Meteorites which have a typical medium and fine structure remain homogeneous to about 475° and 400°C respectively. The kamacite phase in ataxites remain homogeneous below 400°C. In general the typical fine octahedrites and ataxites remain homogeneous to a temperature below 450°C, the temperature at which the maximum Ni solubility in kamacite occurs, while the typical coarse and medium octahedrites become inhomogeneous above 450°C.

From the results of the homogeneity calculations certain predictions about the resultant composition gradients (Figure 4) can be made. These predictions can most easily be discussed by considering the following two cases:

Case I - Average sized kamacite bands, fine octahedrites, ataxites, plessite. For kamacite bands which remain homogeneous below 450°C, with a half width less than 0.1 mm, the Ni concentration in kamacite should vary in the following manner (Figure 4): At T_3, ~ 450°C, the bands have reached a maximum Ni content and are homogeneous. At a lower temperature, T_4, they are homogeneous and have a lower Ni content as given by the phase diagram. At temperature T_5, D_α is so low that Ni cannot diffuse completely from the interior of the kamacite phase to the kamacite/taenite interface. This effect produces a Ni depletion in the kamacite phase near the kamacite/taenite interface.

One can also predict that: (1) As the half width W of kamacite decreases, the average Ni content in kamacite will decrease. In other words the 'average sized kamacite phase' of the ataxites will have lower Ni contents than the 'average sized kamacite phase' in fine octahedrites. (2) Any kamacite plate of half width W will have the same concentration variation and average Ni content no matter what meteorite it is found in.

Case II - Average sized kamacite bands, coarse and medium octahedrites. For kamacite bands which become inhomogeneous above 450°C, with a half width greater than 0.1 mm, the Ni concentration in kamacite should vary in the following manner: At $T_1 \sim 600^\circ C$, the bands are homogeneous with a Ni content given by the equilibrium phase diagram. At T_2, the Ni content as given by the phase diagram must increase. However, the diffusion coefficient is so low that Ni cannot diffuse completely from the kamacite-taenite interface into the interior of the phase. Therefore a Ni gradient occurs. By temperature T_3, the gradient becomes much larger. Below $450^\circ C$, the Ni content at the kamacite-taenite interface begins to decrease. Because of this decrease, a Ni depletion near the α/γ interface forms, T_5. This is the same type of depletion as predicted for the fine octahedrites and the ataxites. The reverse gradient which is predicted to occur from the center of the kamacite phase towards the kamacite/taenite interface has never been reported.

One can further predict that: (1) As the half width W of the kamacite phase decreases, the average Ni content in kamacite will increase. This occurs because the smaller sized kamacite plates become inhomogeneous at a lower temperature. Therefore as the width of the 'average sized kamacite phase' in meteorites decreases from the mm size to the micron size, the average kamacite composition will increase, going from coarse to medium octahedrites (7-10% Ni) and then begin to decrease from the fine octahedrites to the ataxites (10-27% Ni). (2) Any kamacite plate of a half width W will have the same concentration variation and average composition no matter what meteorite it is found in.

Experimental Procedure. Eight meteorites were analyzed with the electron probe. The meteorites and their average Ni contents are listed in Table 2.

TABLE 2

Meteorites analyzed in this study

Meteorite	Average Ni Content (wt %)	Classification	Reference
Smithsonia	5.88	H	Roy and Wyant, 1950
Canyon Diablo	7.18	Og	Lovering, et al, 1956
Carbo	8.68	Om	Palache and Gonyer, 1930
Breece	9.17	Om	Henderson and Perry, 1958
Mount Edith	9.40	Om	Lovering, et al., 1956
Carlton	12.77	Of	Henderson, private communication
Dayton	18.10	A	Henderson and Perry, 1958
Weaver Mountains	18.03	A	Henderson and Perry, 1951

Selected sections of these meteorites were first mounted in bakelite. Before electron-probe microanalysis, the samples were polished through ¼ micron diamond paste, taking special care to be sure that there were no apparent height differences between the α and γ phases. The orientation of the kamacite plates that were analyzed was not determined.

An A. R. L. (Applied Research Laboratories) electron microanalyzer was used to measure the Ni concentrations across the kamacite phases of the meteorites. In making the measurements two important factors were considered: (1) Accuracy-accurate measurement of the true composition of kamacite. (2) Precision-precise measurement of the differences in composition from one point to another in the kamacite phase.

To achieve accurate measurement of the absolute kamacite composition, well analyzed Fe-Ni standards were used. The alloys and the use of these standards has already been described [Goldstein and Ogilvie, 1965c]. To obtain precision of better than 10% one must quantitatively count the X-ray intensity. In this study long counting times were necessary. At least 100,000 counts of Ni were measured insuring that a variation of better than 1 per cent of the amount present at any one point in the kamacite phase could be measured ($3\sigma \sim .05$ wt% Ni). Allowing for the usual instabilities of the electron probe, a more reasonable estimate of precision is ~.1 wt% Ni. The beam stability was checked after every analysis of a kamacite lamellae. If the X-ray intensity varied more than 2% from the standards the data were rejected.

The average composition of a kamacite band was computed in one of two ways: (1) Taking an average of a point to point analysis, across the phase; (2) Taking an average of only a few random points within the phase. Although a complete gradient should be measured, it is estimated that an average of only a few measurements will still yield a value of the average Ni content accurate to .25 wt% Ni.

Results. Several electron probe scans were made across kamacite bands with a half width less than .1mm (Case I). Typical scans across two kamacite bands in the Carlton fine octahedrite are shown in Figure 5. The predicted Ni gradients for Case I are verified. The average composition of the kamacite decreases as the half width decreases from .085 mm to .020 mm.

This variation was also predicted as a result of the diffusion model.

Several electron probe scans were made across kamacite bands of a half width greater than .1 mm (Case II). A scan across a kamacite band in the Canyon Diablo coarse octahedrite is shown in Figure 6. The predicted Ni gradients for Case II are also verified. A scan across a kamacite band in the Breece medium octahedrite is shown in Figure 7. This scan also shows the reverse gradient from the center of the kamacite phase towards the α/γ interface and the interface depletion, starting 50 microns from the interface. From these two figures, one can see as predicted that the average kamacite composition increases for the 'average sized kamacite bands' from the coarse to the medium octahedrites.

Measurements of the average composition of 'averaged sized kamacite plates' were made for the eight meteorites studied. The averaging technique has already been described. These measurements and the measurements of Reed [1964] and Short and Anderson [1964] are plotted versus the overall Ni concentration of the meteorite (Figure 8). The measurements by the other two authors did not include the Ni depletion near the α/γ interface in their averaging process. Therefore their averaging process will yield average Ni concentrations slightly higher than those obtained in this study. The experimental data verifies the prediction that the kamacite composition will increase going from coarse to medium octahedrites (7-10% Ni) and then begin to decrease from the fine octahedrites to the ataxites (10-27% Ni).

The composition of kamacite bands smaller than the 'average sized kamacite bands,' of the meteorite was measured. The results of these analyses are shown in Figure 9 where the average Ni content of the kamacite phase is plotted as a function of the width of the phase. A band is drawn through the data points. The band width represents the uncertainty in the orientation of the kamacite phase with respect to the polished surface and the uncertainty in the measurement of the average Ni content in kamacite. In the Canyon Diablo meteorite (Og), for example, as the size of the kamacite phase decreases from that of the 'average sized band' (>1 mm) the average nickel content in kamacite increases and then decreases. In the Carlton meteorite (Of) as the size of the kamacite phase decreases from that of the average sized band (~.1 mm) the average Ni content in the kamacite decreases. It is interesting to note that for kamacite bands characterized by a half width W, the average composition of the phase is the same no matter what the overall Ni content of the parent meteorite is. This result confirms another prediction which was given as a result of the diffusion model.

Discussion. Predictions of the composition variations in the kamacite phase of metallic meteorites have been made based on a cooling rate of $2^{\circ}/10^{6}$ years and the low pressure Fe-Ni diagram. These predictions have been verified by electron probe microanalysis. The interface depletion in the kamacite phase can now be explained on the basis of the newly determined Fe-Ni diagram [Goldstein and Ogilvie, 1965b]. The prediction of a Ni enrichment from the center of the kamacite phase extending close to the α/γ interface for coarse and medium octahedrites has been verified. This is the first report of such a gradient. An explanation of the variation of the average Ni content of kamacite plates of varying sizes within one meteorite, first reported by Short and Anderson [1964], has been given.

The nickel content of the kamacite phase is not constant. Even if one neglects the interface depletion in kamacite, the kamacite phase is still not homogeneous. Therefore the only place where equilibrium conditions exist in metallic meteorites at low temperatures is at the kamacite/taenite interface. The values of the kamacite and taenite compositions at the kamacite/taenite interface [Reed, 1964] are in substantial agreement with the solubility limits of the new Fe-Ni phase diagram at about 350°C.

The diffusion analysis that was used in this study is based on a number of approximations which limit its accuracy. It does not allow one to estimate the absolute amount of the Ni concentration gradients or their extent. The analysis is consistent with a cooling rate on the order of 1°-$10^{\circ}/10^{6}$ years for the meteorites analyzed in this study. This cooling rate implies either that metallic meteorites are formed in one or several parent asteroidal bodies of the size of 100-250 km in radius, or in isolated metallic areas in a larger parent body cooling at this rate. The results of this investigation provide another piece of evidence for the case of the low pressure origin of meteorites.

Conclusions. On the basis of a diffusion model and the newly determined Fe-Ni phase diagram, the following predictions about the kamacite phase in meteorites are made:

(1) The kamacite phase becomes inhomogeneous during the cooling process.

(2) A Ni depletion near the α/γ interface forms below 450°C.

(3) A concentration gradient from the center of the kamacite phase towards the α/γ interface forms in the 'typical sized kamacite plates' of coarse and medium octahedrites.

(4) A variation in the average Ni content of the 'typical sized kamacite bands' occurs with the overall Ni content of the meteorite.

(5) The average composition of kamacite plates of the same width is the same no matter what the overall Ni content of the parent meteorite is.

These predictions have been confirmed by electron probe measurements of several metallic meteorites. This correlation is in agreement with cooling rates of parent bodies which form at low pressures.

Acknowledgments. The author wishes to thank Dr. L. Walter, Dr. J. Short, and Prof. R. E. Ogilvie for their helpful discussions during the course of this work.

List of Figures

References

Agrell, S. O., J. V. P. Long, and R. E. Ogilvie, Nature, 198, 749, 1963.

Borg, R. J. and D. Y. F. Lai, Acta Met., 11, 861, 1963.

Crank, J., The mathematics of diffusion, Oxford Univ. Press, London, 1956.

Goldstein, J. I. and R. E. Ogilvie, Geochimica et Cosmochimica Acta, to be published 1965a.

Goldstein, J. I. and R. E. Ogilvie, submitted to Trans. Met. Soc. AIME, 1965b.

Goldstein, J. I., and R. E. Ogilvie, Trans. Met. Soc. AIME, 233, 812, 1965c.

Henderson, E. P. and S. H. Perry, Pop. Astron., 59, 263, 1951.

Henderson, E P. and S. H. Perry, Proc. U. S. National Museum, 107, 339, 1958.

Lovering, J. F., W. Nichiporuk, A. Chodos, and H. Brown, Geochimica et Cosmochimica Acta, 11, 263, 1957.

Owen, E. A. and Y. H. Liu, J. Iron Steel Inst., London, 163, 132, 1949.

Palache, C. and F. A. Gonyer, Amer. Min., 15, 388, 1930.

Reed, S. J. B., Private communication, 1964.

Roy, S. K. and R. K. Wyant, Geol. Ser. Field Mus. Nat. Hist., Chicago, 7, 129, 1950.

Short, J. M. and C. A. Anderson, Journal of Geophysical Research, in press, 1965.

Wood, J. A., Icarus, 3, 429, 1964.

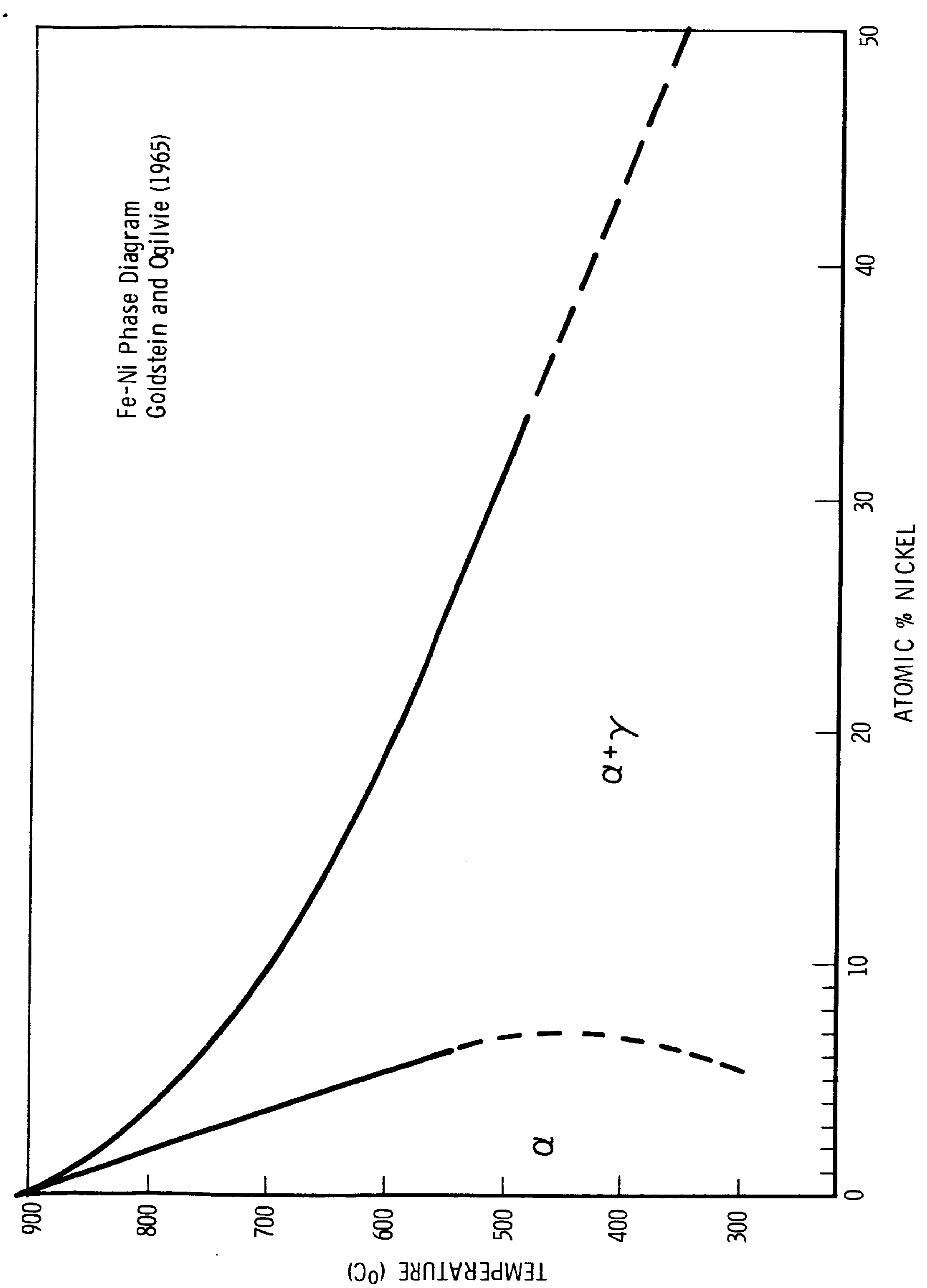
Fe-Ni Phase Diagram
Goldstein and Ogilvie (1965)
α
α+γ
TEMPERATURE (°C)
900
800
700
600
500
400
300
ATOMIC % NICKEL
0
10
20
30
40
50

Figure 1

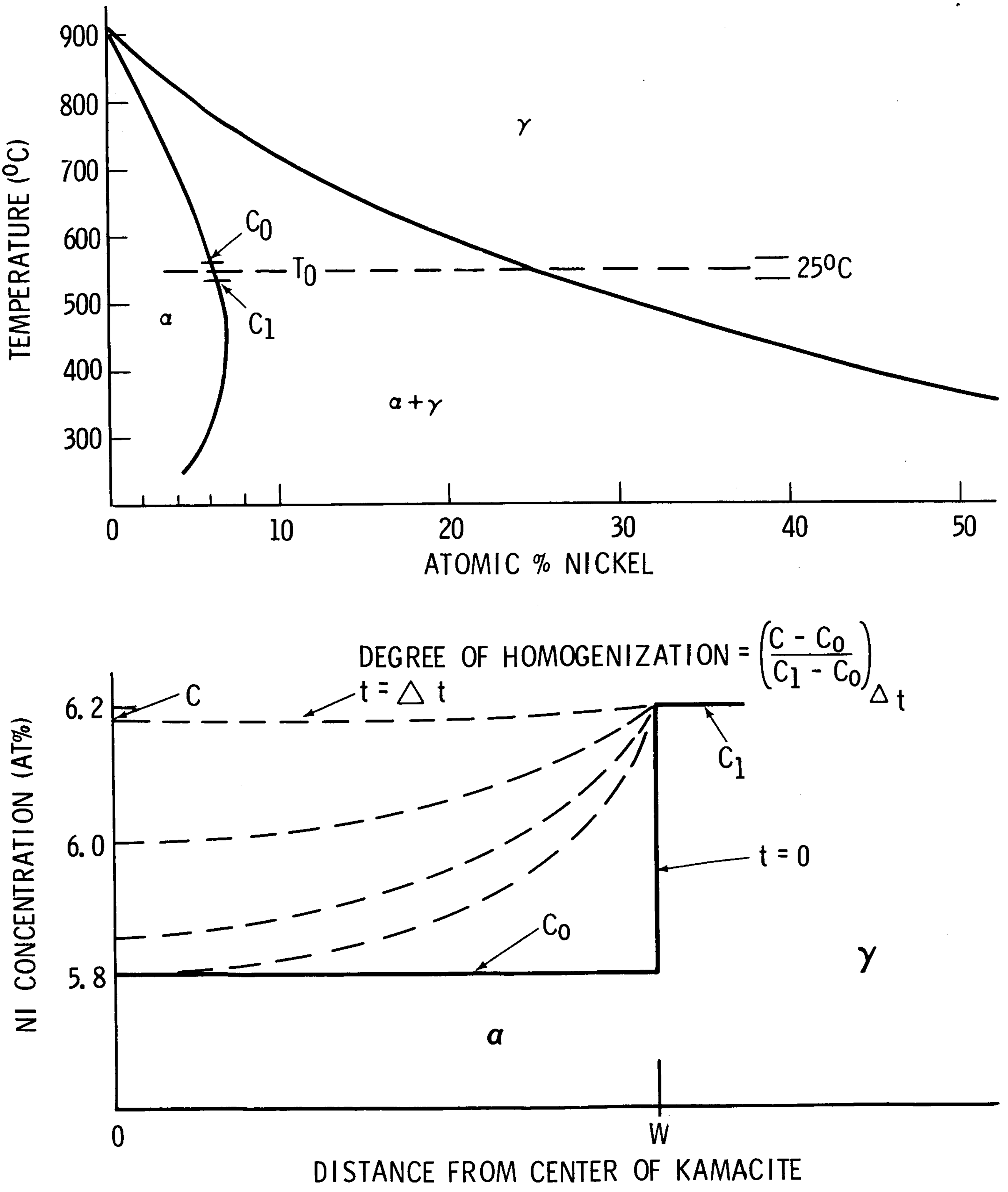
900
800
700
600
500
400
300
TEMPERATURE (°C)
γ
C0
T0
25°C
α
C1
α + γ
0
10
20
30
40
50
ATOMIC % NICKEL
DEGREE OF HOMOGENIZATION = (C - C0 / C1 - C0) Δt
6.2
6.0
5.8
C
t = Δ t
C1
t = 0
C0
γ
α
NI CONCENTRATION (AT%)
0
W
DISTANCE FROM CENTER OF KAMACITE

Figure 2

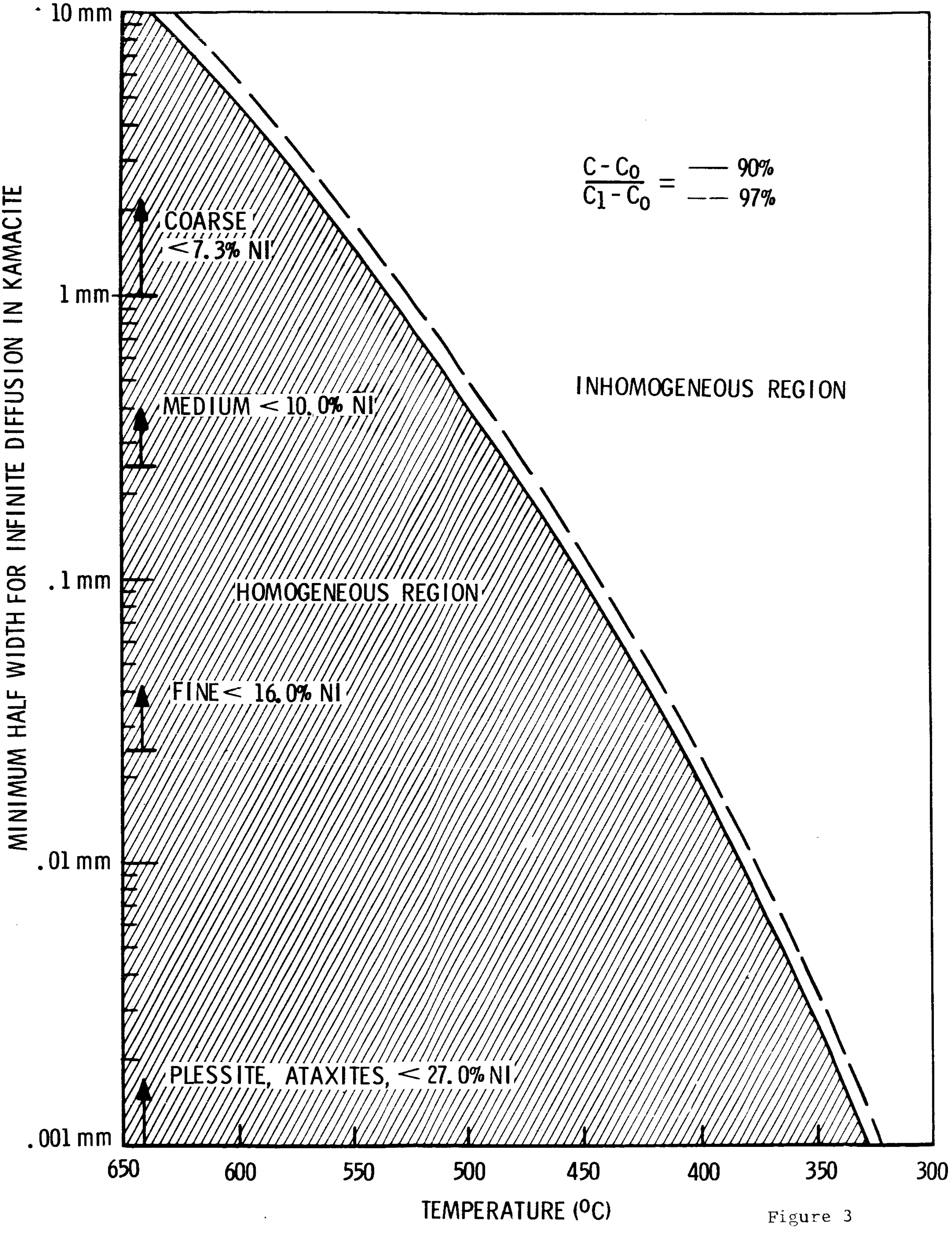
10 mm
1 mm
.1 mm
.01 mm
.001 mm
MINIMUM HALF WIDTH FOR INFINITE DIFFUSION IN KAMACITE
650
600
550
500
450
400
350
300
TEMPERATURE (°C)
C - C0 / C1 - C0 = —— 90% / — — 97%
COARSE <7.3% NI
MEDIUM < 10.0% NI
FINE < 16.0% NI
PLESSITE, ATAXITES, < 27.0% NI
HOMOGENEOUS REGION
INHOMOGENEOUS REGION

Figure 3

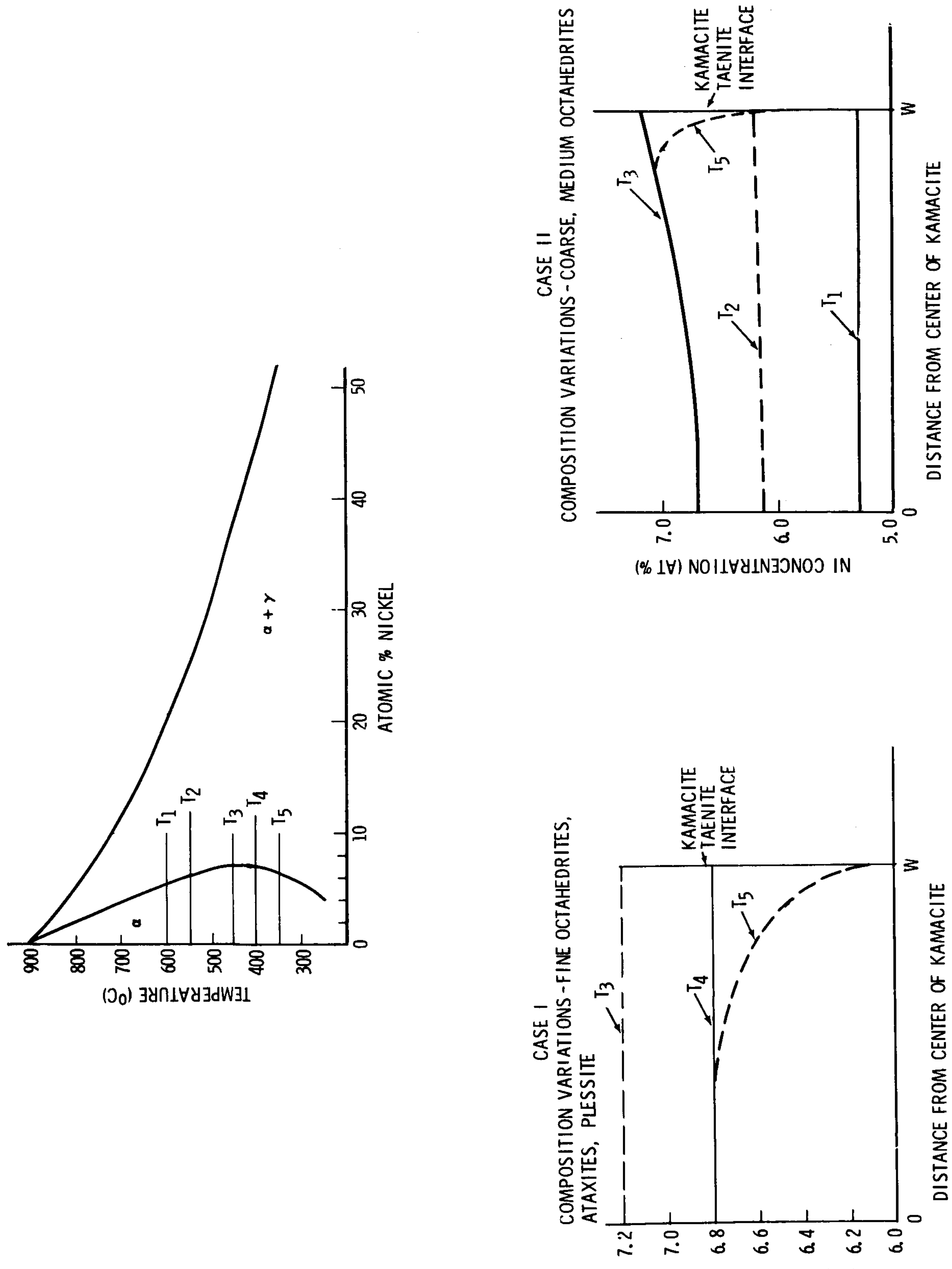
TEMPERATURE (°C)
900
800
700
600
500
400
300
ATOMIC % NICKEL
0
10
20
30
40
50
α
α + γ
T1
T2
T3
T4
T5
CASE I
COMPOSITION VARIATIONS - FINE OCTAHEDRITES,
ATAXITES, PLESSITE
NI CONCENTRATION (AT%)
7.2
7.0
6.8
6.6
6.4
6.2
6.0
0
W
DISTANCE FROM CENTER OF KAMACITE
T3
T4
T5
KAMACITE
TAENITE
INTERFACE
CASE II
COMPOSITION VARIATIONS - COARSE, MEDIUM OCTAHEDRITES
NI CONCENTRATION (AT %)
7.0
6.0
5.0
0
W
DISTANCE FROM CENTER OF KAMACITE
T1
T2
T3
T5
KAMACITE
TAENITE
INTERFACE

Figure 4

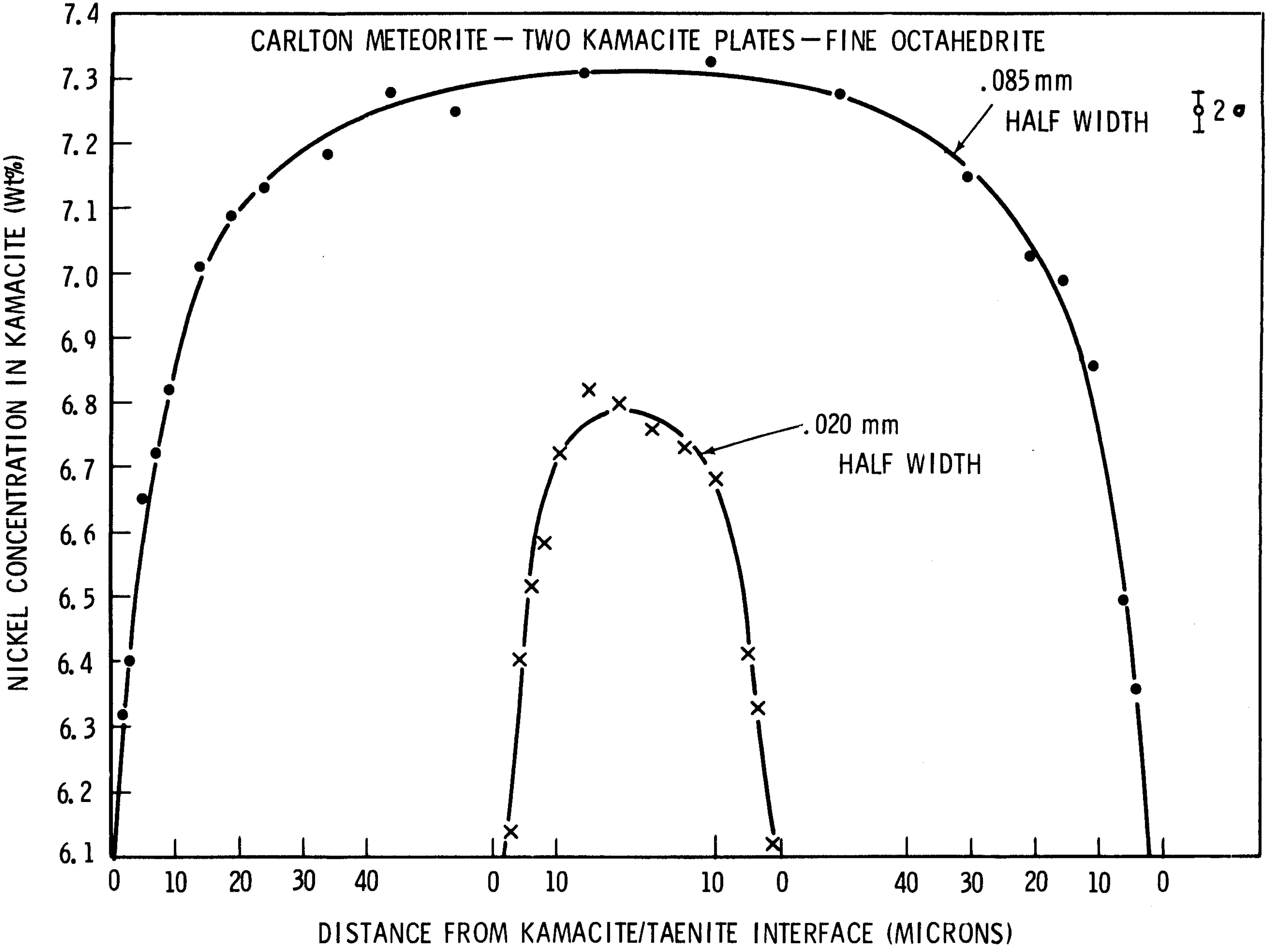
CARLTON METEORITE — TWO KAMACITE PLATES — FINE OCTAHEDRITE
.085 mm
HALF WIDTH
.020 mm
HALF WIDTH
2σ
NICKEL CONCENTRATION IN KAMACITE (Wt%)
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
0
10
20
30
40
0
10
10
0
40
30
20
10
0
DISTANCE FROM KAMACITE/TAENITE INTERFACE (MICRONS)

Figure 5

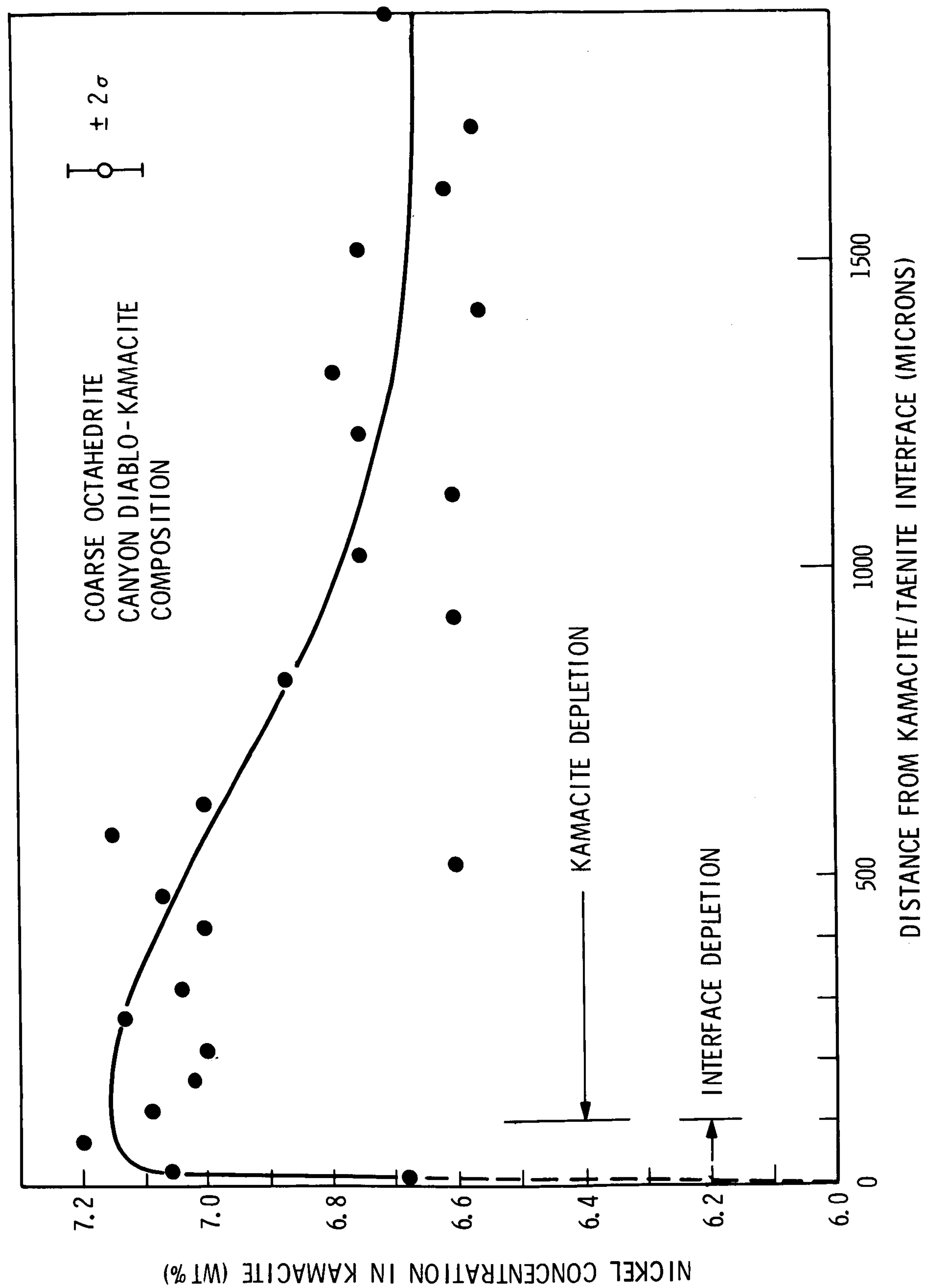
COARSE OCTAHEDRITE
CANYON DIABLO-KAMACITE
COMPOSITION
± 2σ
KAMACITE DEPLETION
INTERFACE DEPLETION
NICKEL CONCENTRATION IN KAMACITE (WT %)
7.2
7.0
6.8
6.6
6.4
6.2
6.0
DISTANCE FROM KAMACITE/TAENITE INTERFACE (MICRONS)
0
500
1000
1500

Figure 6

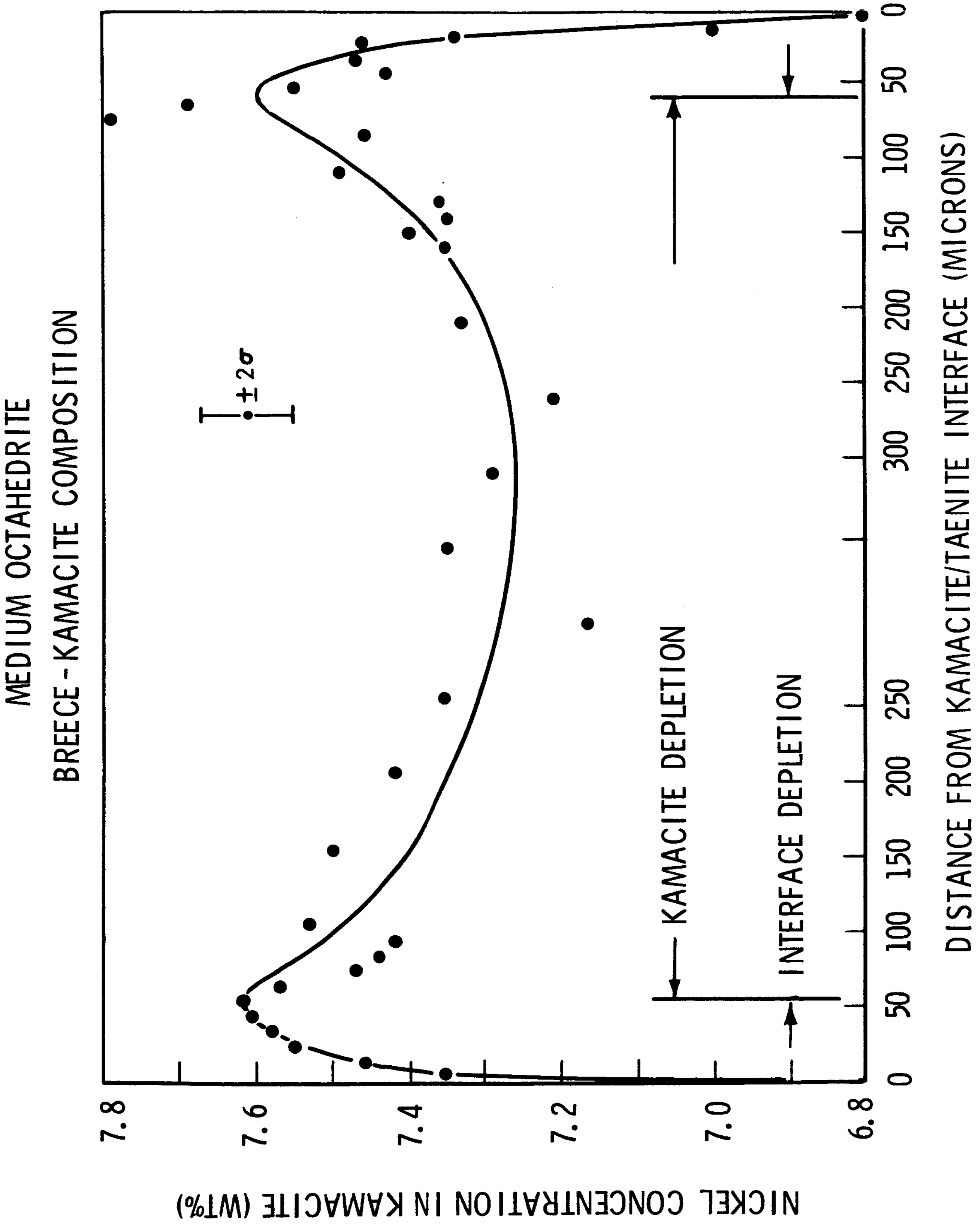
MEDIUM OCTAHEDRITE
BREECE-KAMACITE COMPOSITION
±2σ
KAMACITE DEPLETION
INTERFACE DEPLETION
7.8
7.6
7.4
7.2
7.0
6.8
NICKEL CONCENTRATION IN KAMACITE (WT%)
0
50
100
150
200
250
300
250
200
150
100
50
0
DISTANCE FROM KAMACITE/TAENITE INTERFACE (MICRONS)

Figure 7

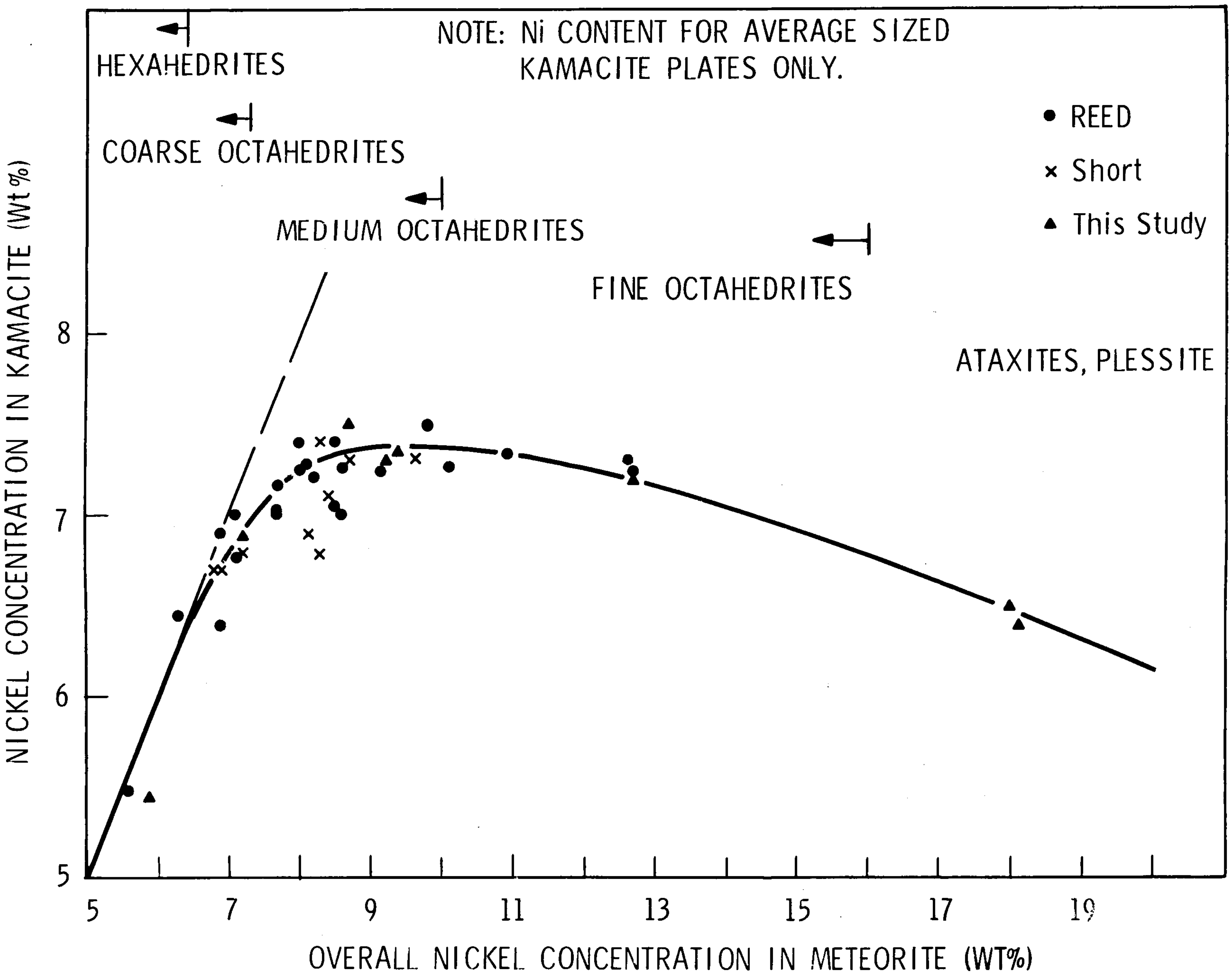
NOTE: Ni CONTENT FOR AVERAGE SIZED KAMACITE PLATES ONLY.
HEXAHEDRITES
COARSE OCTAHEDRITES
MEDIUM OCTAHEDRITES
FINE OCTAHEDRITES
ATAXITES, PLESSITE
● REED
× Short
▲ This Study
NICKEL CONCENTRATION IN KAMACITE (Wt%)
5
6
7
8
OVERALL NICKEL CONCENTRATION IN METEORITE (WT%)
5
7
9
11
13
15
17
19

Figure 8

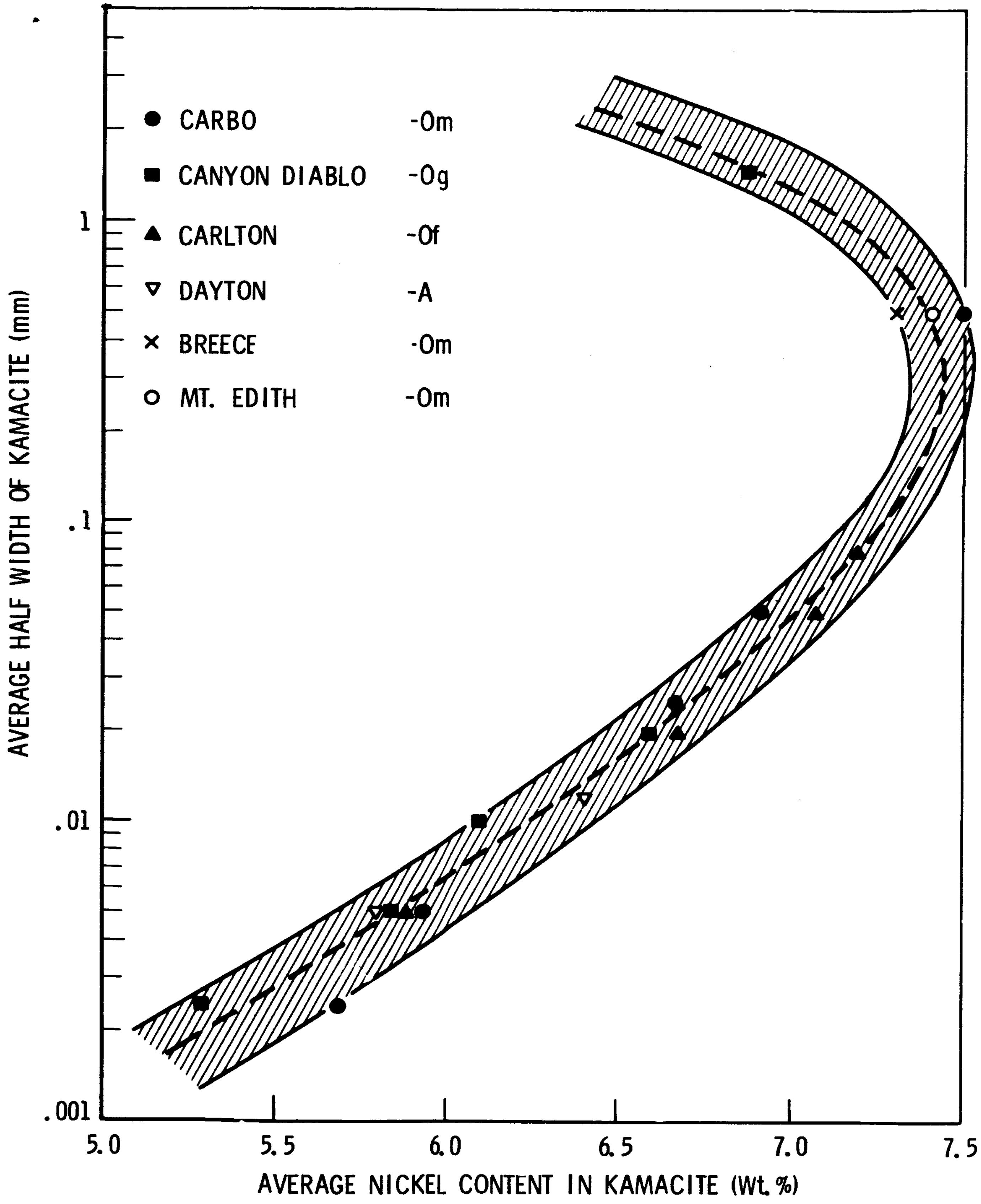
● CARBO -Om
■ CANYON DIABLO -Og
▲ CARLTON -Of
▽ DAYTON -A
× BREECE -Om
○ MT. EDITH -Om
AVERAGE HALF WIDTH OF KAMACITE (mm)
1
.1
.01
.001
5.0
5.5
6.0
6.5
7.0
7.5
AVERAGE NICKEL CONTENT IN KAMACITE (Wt. %)

Figure 9