CONF-780493--6

2

MASTER

DECARBURIZATION OF 2-1/4Cr-1Mo IN FLOWING SODIUM

P. Roy and C.N. Spalaris (GE), S. Kano (PNC)
Japan/U.S Specialists

Meeting on "Materials Behavior in Sodium and Cover Gas"
April 17-20, 1978
Chicago, Ill

DECARBURIZATION OF 2-1/4Cr-1Mo IN FLOWING SODIUM

P. Roy and C.N. Spalaris (GE), S. Kano (PNC)
Japan/U.S Specialists

Meeting on "Materials Behavior in Sodium and Cover Gas"
April 17-20, 1978

The Intermediate System Mock-up Sodium Loop (ISML) was designed to model a bi-metallic (austenitic stainless steel and 2-1/4Cr-1Mo ferritic steel) LMFBR intermediate heat transport system. This loop has operated for about 11,000 hours with a projected objective to establish the decarburization kinetics for 2-1/4Cr-1Mo and carburization rates for Types 304 and 316 stainless, operative in an intermediate heat transport sodium loop. Details of the loop construction were published in Reference 1.

Melting Practice As It Affects Decarburization Rates

Alloy 2-1/4Cr-1Mo prepared by the vacuum arc remelt (VAR) and electroslag remelt (ESR) processes were tested and results obtained for periods up to 7,200 hours are reported in this memorandum. Even though the VAR and the ESR samples were taken from an identical air melted ingot, the VAR exhibited 2-15 times higher decarburization rates than ESR at all test temperatures. Activation energies derived from plotting the decarburization constant against the reciprocal temperature were 5K cal/mole for VAR and 24K cal/mole for the ESR. Differences have been tentatively ascribed to silicon content and other minor elements which control the composition of carbides in the alloy matrix.

Geometry Effects

Decarburization constants have been calculated using the following expression: $K=\frac{\Delta C \cdot W}{A\sqrt{t}}$, where ΔC is the change in bulk carbon as a result of carbon loss into the flowing sodium, W the weight of the sample in grams, A the area of the sample exposed in cm^2 and t, time of exposure in seconds.

Decarburization constants for the 10 mil thick tubular foil samples were found to be lower than the K's for the 109 mil thick tubular samples. However, since the activation energies were found to be identical, it is concluded that the carbon loss process is identical for both thicknesses. When the volume of the sample was introduced into the decarburization constant, now defined as K^1 (Prime), $K^1 = \frac{\Delta C \cdot \rho}{\sqrt{t}}$, where ρ is the density, all data from foils and tubes coincided. The geometry effect was found to be the same for both VAR and ESR samples.

Time Dependence

Decarburization constants K and K^1 decrease as a function of time for both foil and thick tubular samples. The rate of slowdown in K and K^1 is greater for the ESR samples. The slowdown rates are proportional to t^x for the VAR (x=0.21) and t^y for the ESR (y=0.46).

Carburization Rates for Type 304 Stainless

Carburization rates in the ISML were found to be lower than the previous data band which contains static pot as well as data from flowing loops. The carburization constants ($K = gm/cm^2 - \sqrt{sec}$) for Type 304 stainless are also found to be independent of exposure temperatures in sodium. This latter observation agrees with data obtained at Cadarash, France.

Heat Treatments Versus Decarburization

It has been hypothesized, but not proven by experiment prior to 1976, that heat treatment of 2-1/4Cr-1Mo was a key factor in influencing the rate of decarburization in sodium. As mentioned earlier in this report, rates of decarburization are time dependent. This relatively new evidence points out that stability of carbides (carbide dissolution) is the rate determining step in the long term decarburization kinetics. Thus, the exact details of heat treatment prior to sodium exposure, both in terms of temperature and time are very important parameters. These facts have not been appreciated by many experimenters, simply because decarburization rates were generally thought to involve simple diffusion processes for carbon in the alloy matrix. Claims that normalized and tempered heat treatment produce microstructures which are more decarburization resistant than "isothermal anneal" are not based on the facts presented in Reference 2 or 3. For example, in Ref. 2, an "anneal" is given a 920°C + 725°C x 1 hour, followed by an air cool. One hour at 725°C will result in a structure predominantly austenite plus ferrite, and most likely, no pearlite. This microstructure will be rich in carbon, and if not tempered by further exposures above 1250°F (to produce stable carbides), will allow the carbon to diffuse quickly into the sodium. When Matsumoto et al., in Ref. 2, applied an extra step to their "annealed" heat treatment (PHT), they obtained decarburization rates lower than the rates exhibited by their normalized and tempered specimens.

Another, more recent reference (3) claims that the "isothermal anneal" produces high decarburization rate structures in 2-1/4Cr-1Mo. This conclusion is apparently based on Heat Treatment III, m, in Ref. 3 which does not specify precise temperature control when the specimens are removed from the furnace at 950°C and transferred into the salt bath. To accomplish this precisely, it would have been necessary to rig the salt bath to receive the specimens directly from the furnace so as to avoid a drop in temperature below 700°C. It is possible that specimens treated in Type III, m, Ref. 3, did not contain the desired ferrite plus carbide, but contained substantial amounts of unstable austenite.

A detailed treatment of the data from Ref. 3 indicates that decarburization rate constants when calculated as per the GE method, fall entirely within the scatter of all existing data.

Neither Ref. 2 nor 3 prove that decarburization rates for normalized and tempered material are lower than the decarburization rates expected in the CRBRP, nor lower than the decarburization rates experienced from ongoing test programs in the Intermediate System Mock-up Loop (ISML). The specimens in the ISML contain only prototypic heat treatments for the CRBRP, and only welded specimens are normalized and tempered. Nevertheless, we see no unusual behavior from the latter as they exhibit decarburization rates which fall within the scatter of all data. The ISML total exposure time now exceeds 11,000 hours as compared to Ref. 2 and 3 which do not exceed 3,900 hours. As shown in several Figures of this memorandum, ESR material exhibits decarburization rates lower by factors of 2 to 10 than VAR and air melted material, even though both types of specimens were taken from the same original air melt. We, therefore, believe this observation to be far more significant than the differences which may exist between the decarburization rate of normalized and tempered versus isothermally annealed material. We suspect silicon content and carbide chemical compositions to be responsible for this observation and we are in close communciation with researchers at Berkeley, CEGB, UK, who also believe this to be a valid explanation based on work they did in the past.

References

1. Steam Generator Materials Engineering - Fourth Quarterly Report, GEAP-14029-4, July 1975 and Krankota, J.L. and Challenger, K., "Carbon Transport and Material Property Degradation in a Model of The Clinch River Breeder Reactor Secondary Sodium System", International Conference on Liquid Metal Technology in Energy Production, Champion, Pa., May 3, 1976.

2. Matsumoto, K. et al., "Carbon Transfer Behavior of Materials for Liquid Metal Fast Breeder Reactor Steam Generators", Nucl. Tech., Vol. 28, March 1976.

3. Transactions of BNES (British Nuclear Energy Society) International Conference on Ferritic Steels for Fast Reactor Steam Generators. Paper No. 45, by P.L.F. Radamakers and B.H. Kolster, June 7, 1977.

VU - GRAPHS

DECARBURIZATION STUDIES

(ISML)

- ENVIRONMENT

  (A) FLOWING SODIUM
  1 TO 2 METERS/SECOND, LESS THAN 2 PPM
  OXYGEN CONTENT (COLD TRAP 121°C).

  (B) TEST TEMPERATURE
  343°C TO 524°C

  (C) SAMPLE GEOMETRY
  TUBULAR FOILS AND CRBRP PROTOTYPIC TUBES.

  (D) BIMETALLIC RATIO OF LOOP COMPONENTS
  PROTOTYPIC CRBRP, 1.7 FERRITIC TO
  AUSTENITIC MATERIALS SURFACE.

- CARBON ANALYSIS

  BULK CARBON, COMBUSTIMETRIC (LECP)

- EXPOSURE TIMES

  UP TO 11,000 HOURS. DATA ANALYZED TO
  7,000 HOURS.

MELTING PRACTICE AS IT AFFECTS DECARBURIZATION IN FLOWING SODIUM

- <u>TYPE OF MELTING PRACTICE</u>

  ELECTROSLAG REMELT AND VACUUM ARC REMELT SAMPLES USED, WHICH ORIGINATED FROM THE IDENTICAL AIR MELTED INGOT.

- <u>SAMPLE GEOMETRY</u>

  CYLINDRICAL FOIL

- <u>EXPOSURE TIME</u>

  7300 HOURS

- <u>HEAT TREATMENT</u>

  ISOTHERMAL ANNEAL, REFERENCE CRBRP

  ANNEAL AT 929°C, 45 MINUTES
  DIRECTLY COOLED TO 710°C, 2 HOURS
  THEN COOLED TO ROOM TEMPERATURE
  THEN 727°C FOR 1 HOUR,
  COOL TO ROOM TEMPERATURE

  ALL ABOVE DONE IN ARGON ATMOSPHERE.

MELTING PRACTICE

- DECARBURIZATION RATE OF VAR IS HIGHER THAN THAT OF ESR BY 2-1/2 TO 15 TIMES DEPENDING UPON TEMPERATURE OF EXPOSURE.

- ACTIVATION ENERGIES ARE 5K CAL/MOLE FOR VAR AND 24K CAL/MOLE FOR ESR.

- DIFFERENCES ARE BELIEVED TO BE DUE TO SILICON CONTENT AND/OR OTHER MINOR ELEMENTS WHICH CONTROL THE COMPOSITION OF CARBIDES IN THE ALLOY MATRIX. (CARBIDE ANALYSIS IN PROGRESS.)

GEOMETRY EFFECTS

- DECARBURIZATION CONSTANTS K FOR FOIL SAMPLES (10 MILS) ARE ALWAYS APPROXIMATELY 5 TIMES LOWER THAN THE K's FOR TUBULAR SAMPLES.

$$K = \frac{\Delta C \cdot W}{A \cdot \sqrt{T}}$$

W = SAMPLE WEIGHT IN GMS

T = TIME IN SECONDS

A = AREA EXPOSED IN CM^2

- ACTIVATION ENERGIES ARE IDENTICAL FOR FOILS AND TUBES. THUS, DECARBURIZATION PROCESS IS IDENTICAL.

- ON THE BASIS OF ABOVE, VOLUME WAS INTRODUCED IN THE DECARBURIZATION CONSTANT, NOW DEFINED AS K^1 (PRIME), EQUAL TO $\frac{\Delta C \cdot \rho}{\sqrt{T}}$

ΔC = CHANGE IN BULK* CARBON CONTENT

ρ = DENSITY GM/CM^3

t = TIME IN SECONDS

- NORMALIZED DATA WITH K^1 SHOWS DATA FROM TUBES AND FOILS TO COINCIDE.

- THE ABOVE STATEMENTS ARE EQUALLY VALID FOR ESR AND VAR SAMPLES.

---

*CROSS SECTION OF TUBULAR WALL.

DECARBURIZATION CONSTANT

TIME DEPENDENCE

- K AND K^1 DECREASE AS A FUNCTION OF TIME, FOR BOTH FOILS AND TUBES.

- THE RATE OF SLOWDOWN IN K AND K^1 IS GREATER FOR THE ESR SAMPLES THAN THAT FOR THE VAR SAMPLES.

- SLOWDOWN RATES ARE PROPORTIONAL TO τ^X FOR VAR AND τ^Y FOR ESR.

$X = 0.21$

$Y = 0.46$

CARBURIZATION RATES FOR TYPE 304 STAINLESS

- CARBURIZATION RATES IN ISML ARE FOUND TO BE LOWER THAN IN PREVIOUS DATA BAND.

- CARBURIZATION CONSTANTS* ARE FOUND TO BE INDEPENDENT OF TEMPERATURE EXPOSURES IN SODIUM.

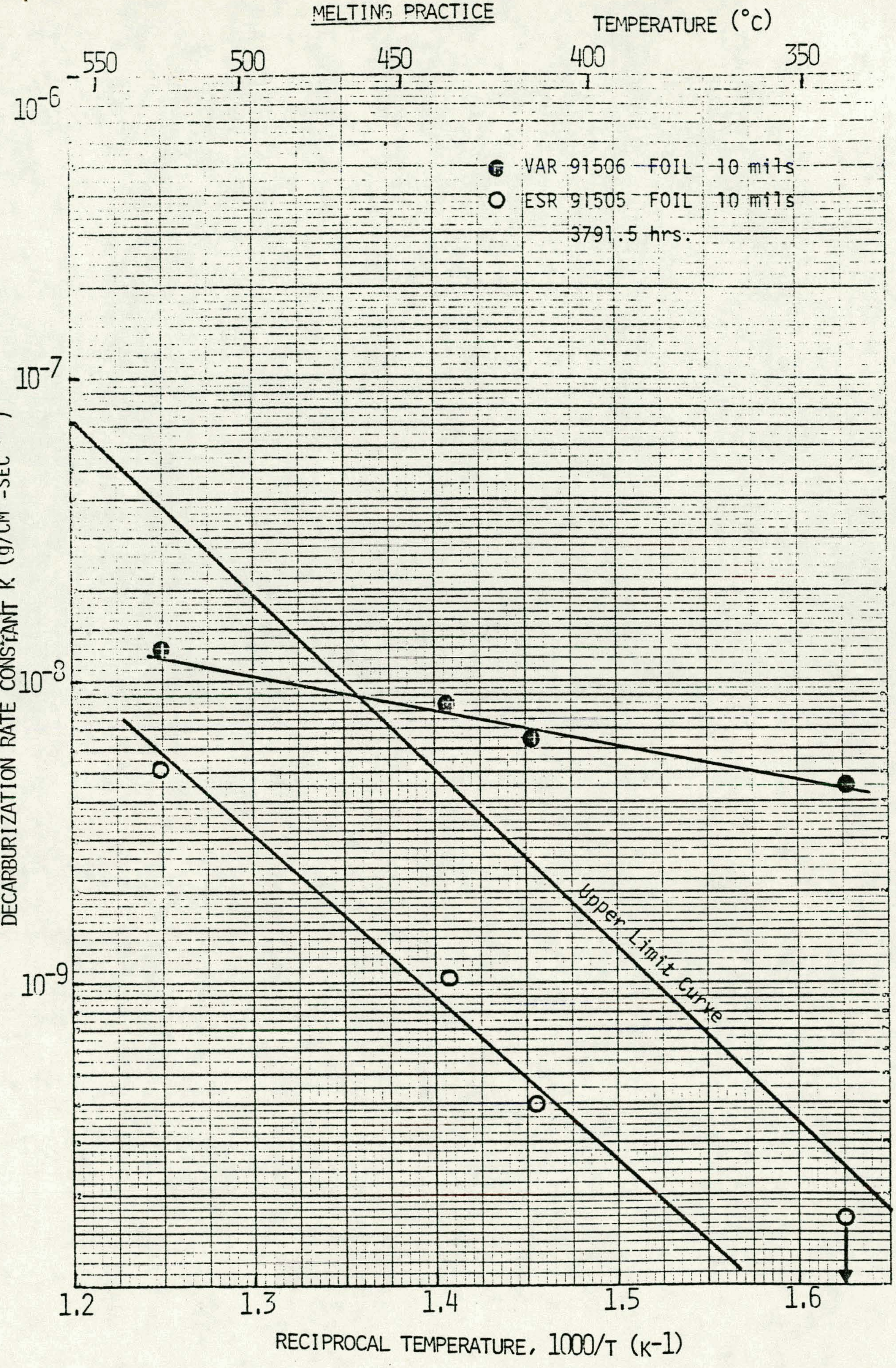
---

*$K = GM/GM^2 - \sqrt{SEC}$

CHEMICAL COMPOSITIONS OF TUBES AND FOILS

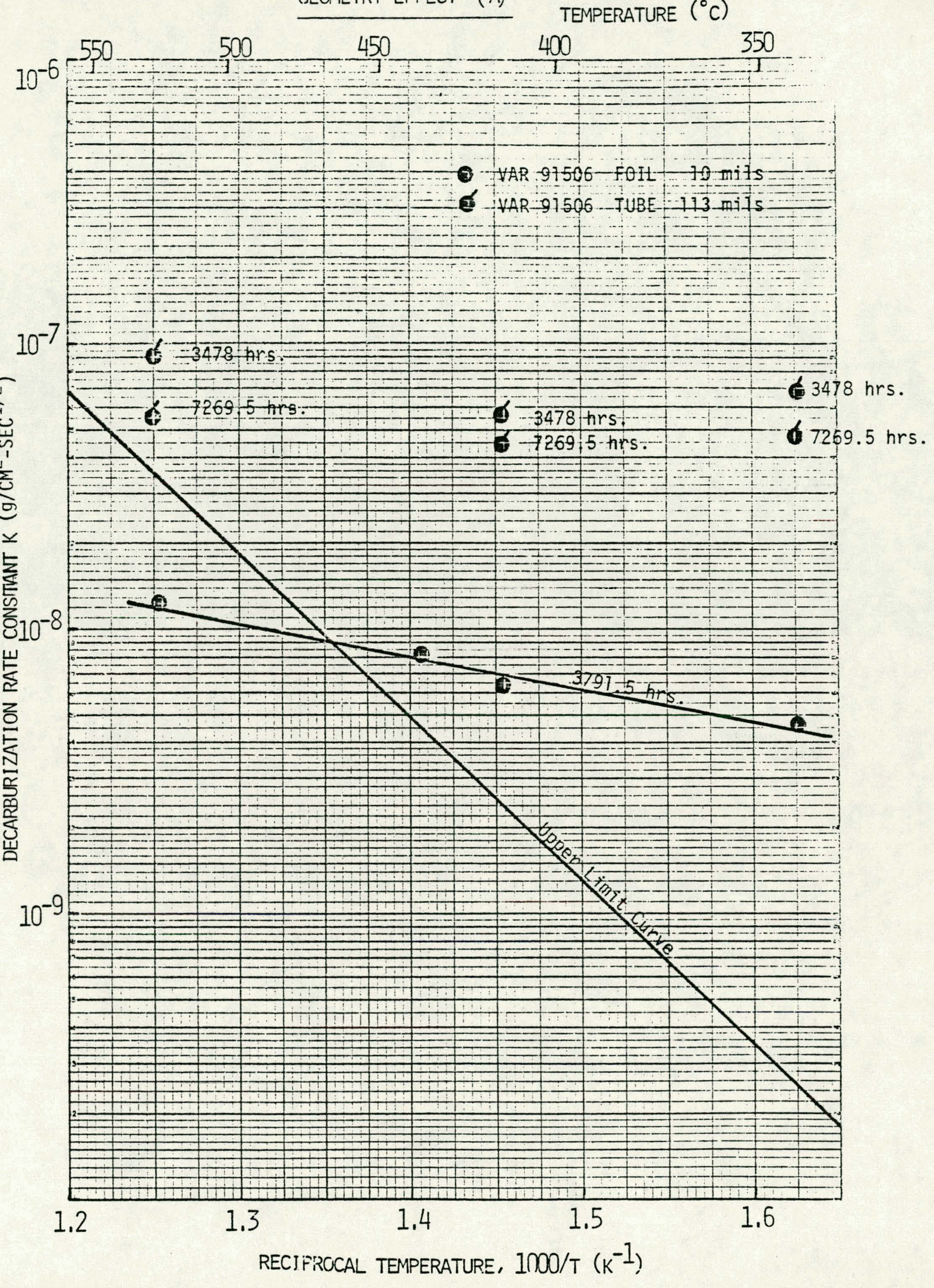
	C* (ppm)	Mn	Cr	Mo	Si	P (w/o)	S	Ni	Cu	Ti	V
VAR 91506 (TUBE)	986.5	0.43	2.31	1.0	0.35	0.007	0.006	0.06	0.05	< 0.01	∿ 0.01
ESR 91505 (TUBE)	980.5	0.46	2.31	1.0	0.26	0.007	0.004	0.05	0.05	< 0.01	∿ 0.01
ESR C1005 (CRBRP ref. tubing)	995	0.44	2.26	1.0	0.19	0.010	0.008	0.19	0.10	< 0.01	< 0.01
VAR 91506 (FOIL)	1105	0.43	2.31	1.0	0.35	0.007	0.006	0.06	0.05	< 0.01	∿ 0.01
ESR 91505 (FOIL)	894	0.46	2.31	1.0	0.26	0.007	0.004	0.05	0.05	< 0.01	∿ 0.01
ESR C1005 (FOIL)	1085	0.44	2.26	1.0	0.19	0.010	0.008	0.19	0.10	< 0.01	< 0.01

*LECO analysis

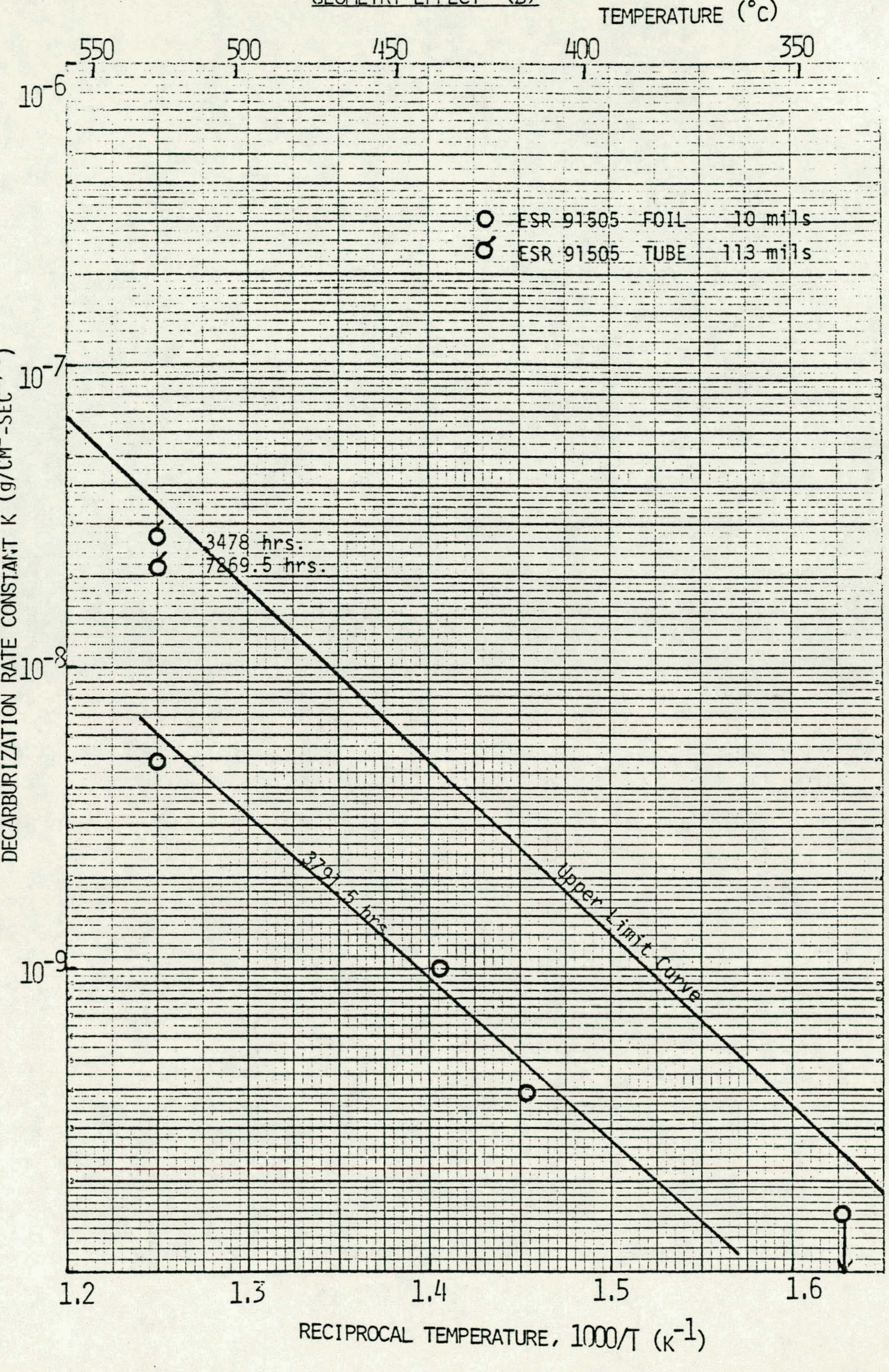


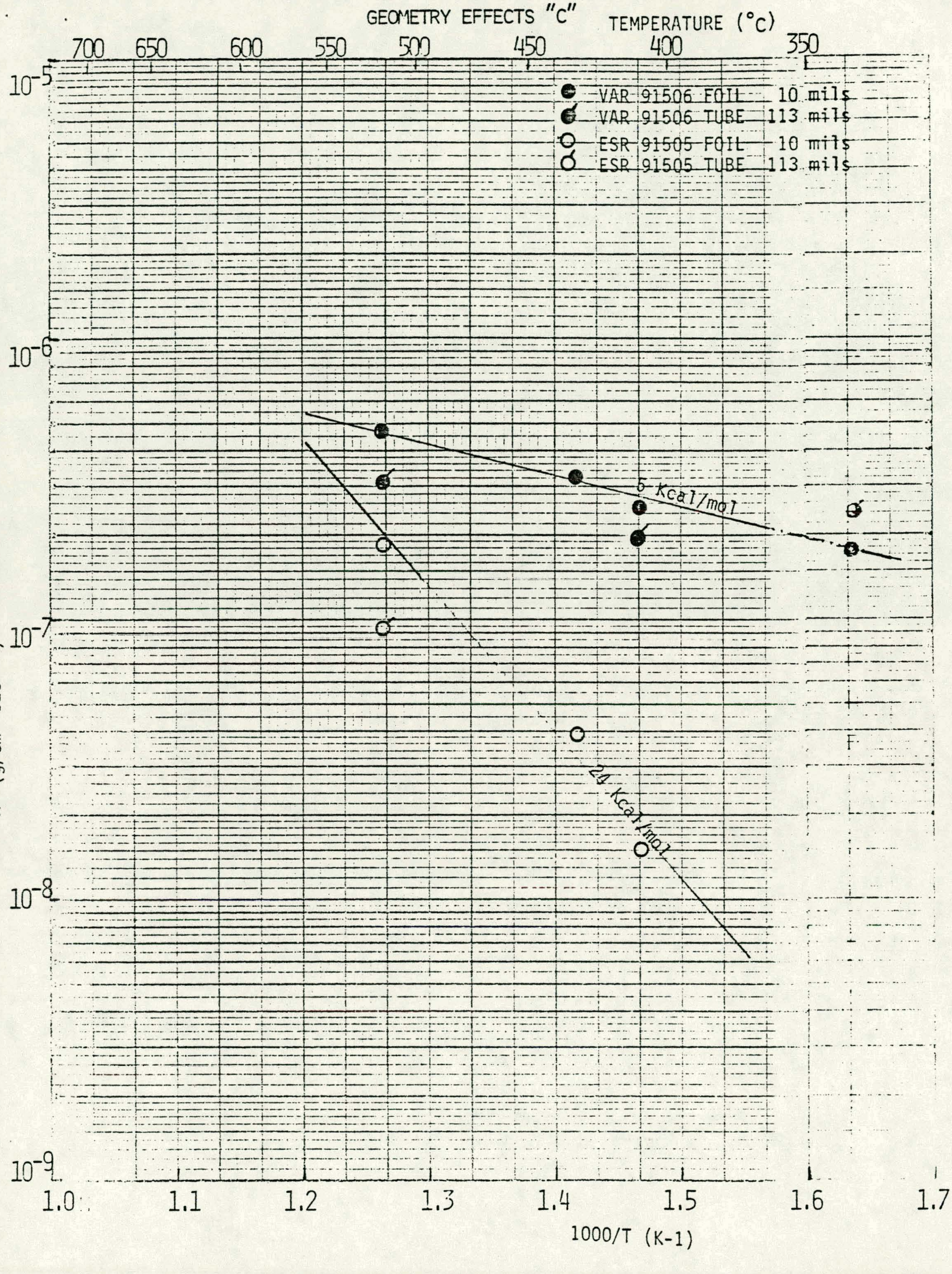
MELTING PRACTICE
TEMPERATURE (°C)
550
500
450
400
350
10-6
10-7
10-8
10-9
VAR 91506 FOIL 10 mils
ESR 91505 FOIL 10 mils
3791.5 hrs.
Upper Limit Curve
DECARBURIZATION RATE CONSTANT K (g/CM2-SEC1/2)
1.2
1.3
1.4
1.5
1.6
RECIPROCAL TEMPERATURE, 1000/T (K-1)

GEOMETRY EFFECT (A)

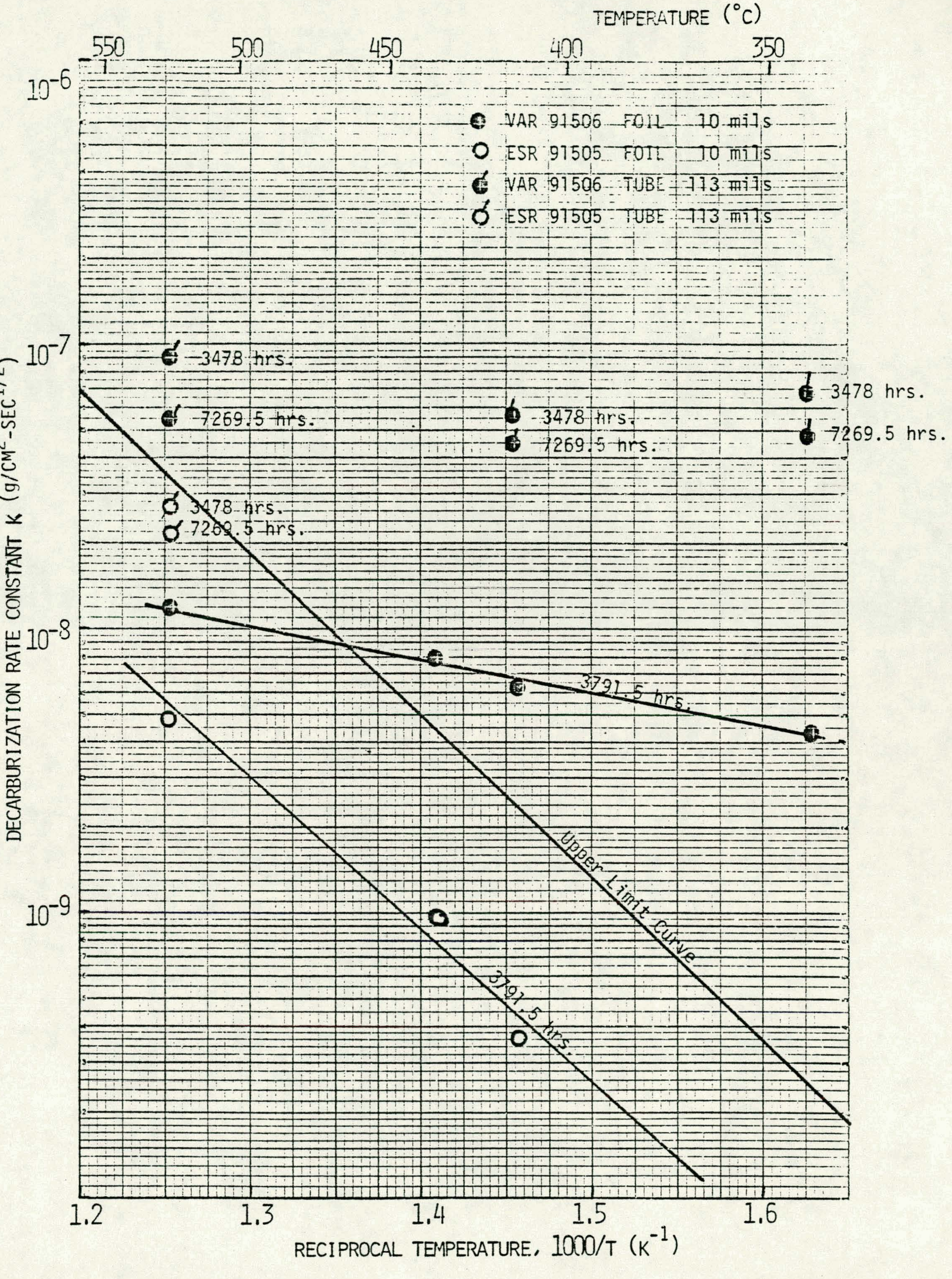


GEOMETRY EFFECT (B)

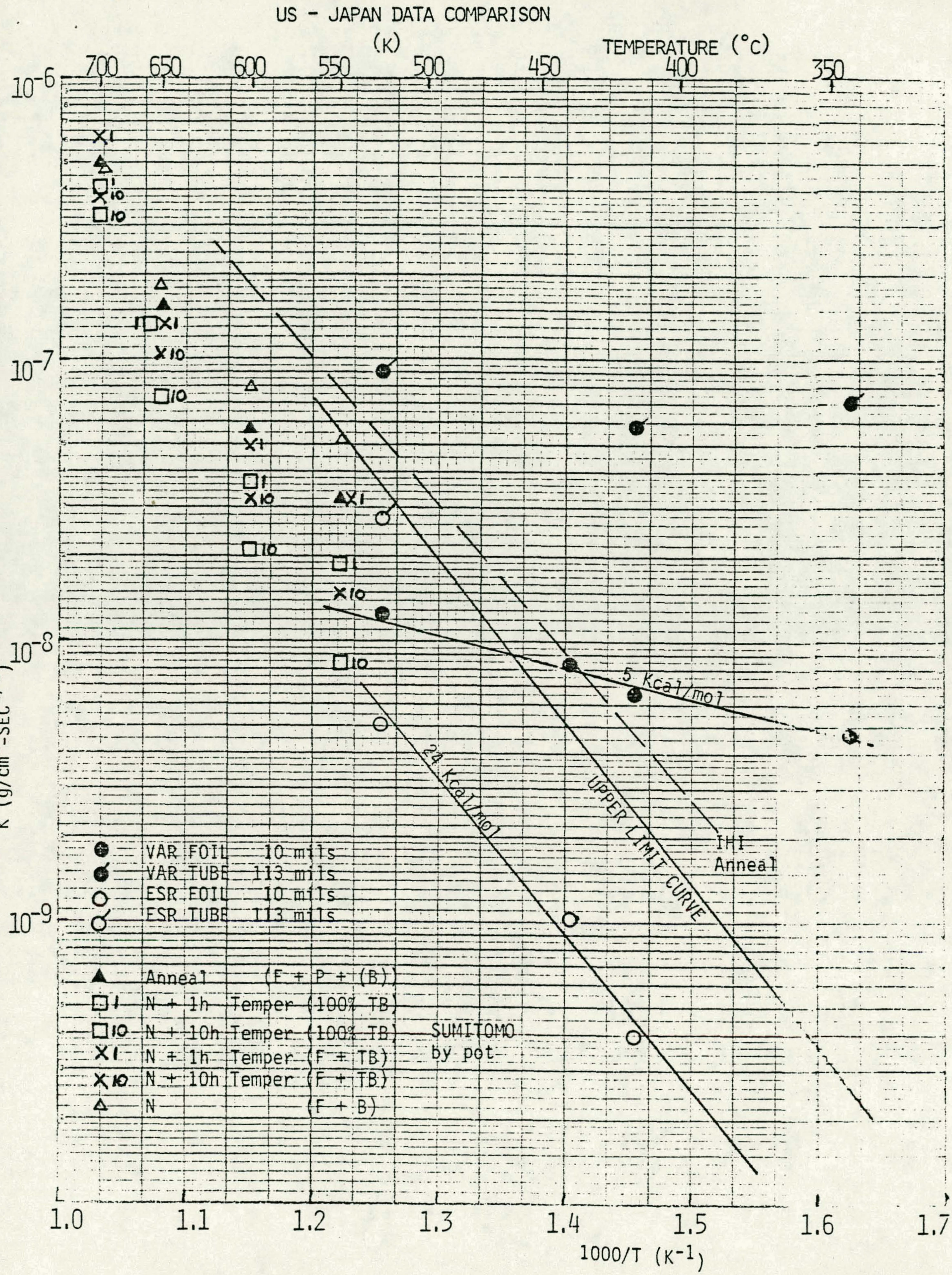




GEOMETRY EFFECTS "C"
TEMPERATURE (°C)
700
650
600
550
500
450
400
350
VAR 91506 FOIL 10 mils
VAR 91506 TUBE 113 mils
ESR 91505 FOIL 10 mils
ESR 91505 TUBE 113 mils
6 Kcal/mol
24 Kcal/mol
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
K^1 $(g/cm^3 - SEC^{1/2})$
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1000/T (K-1)

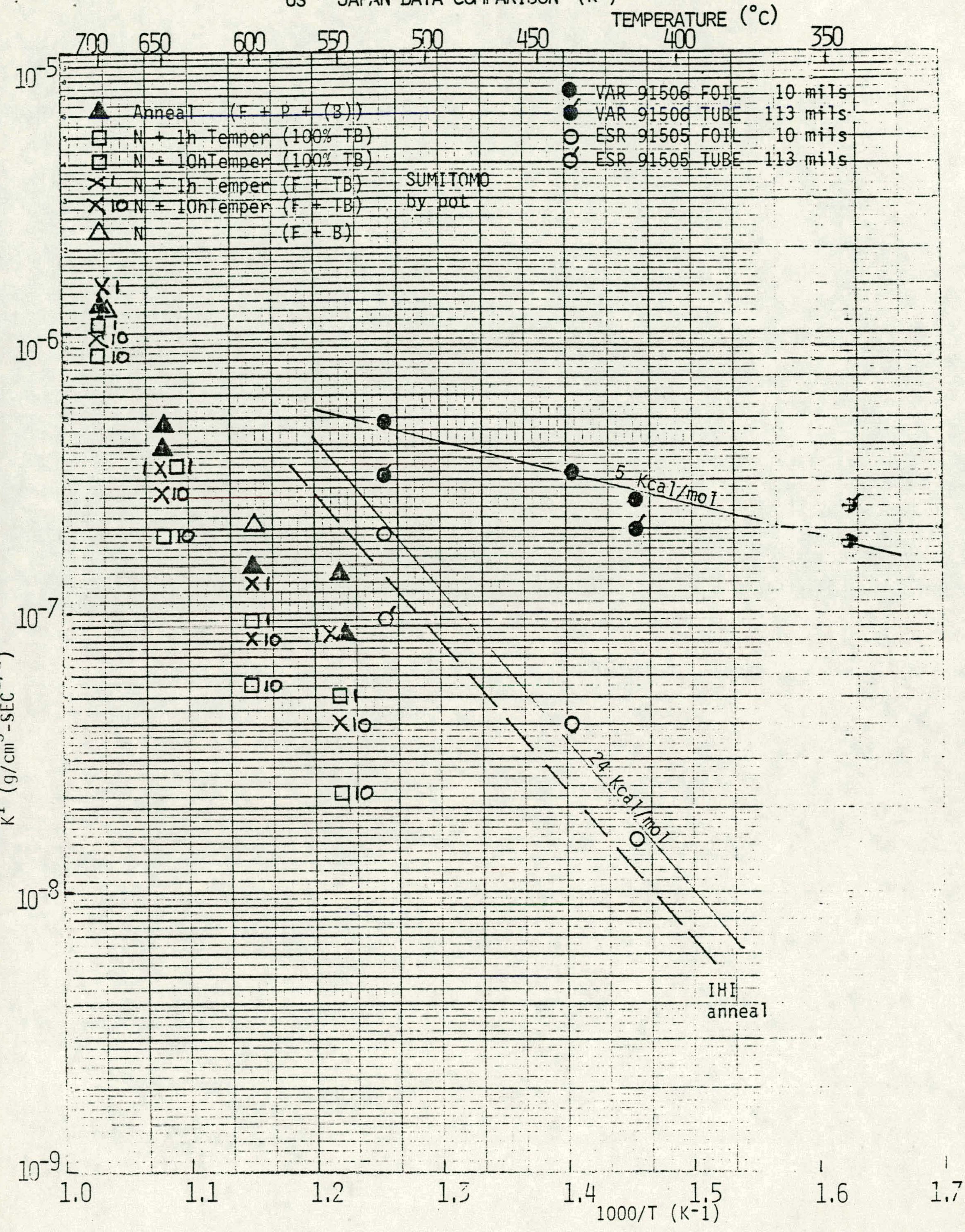


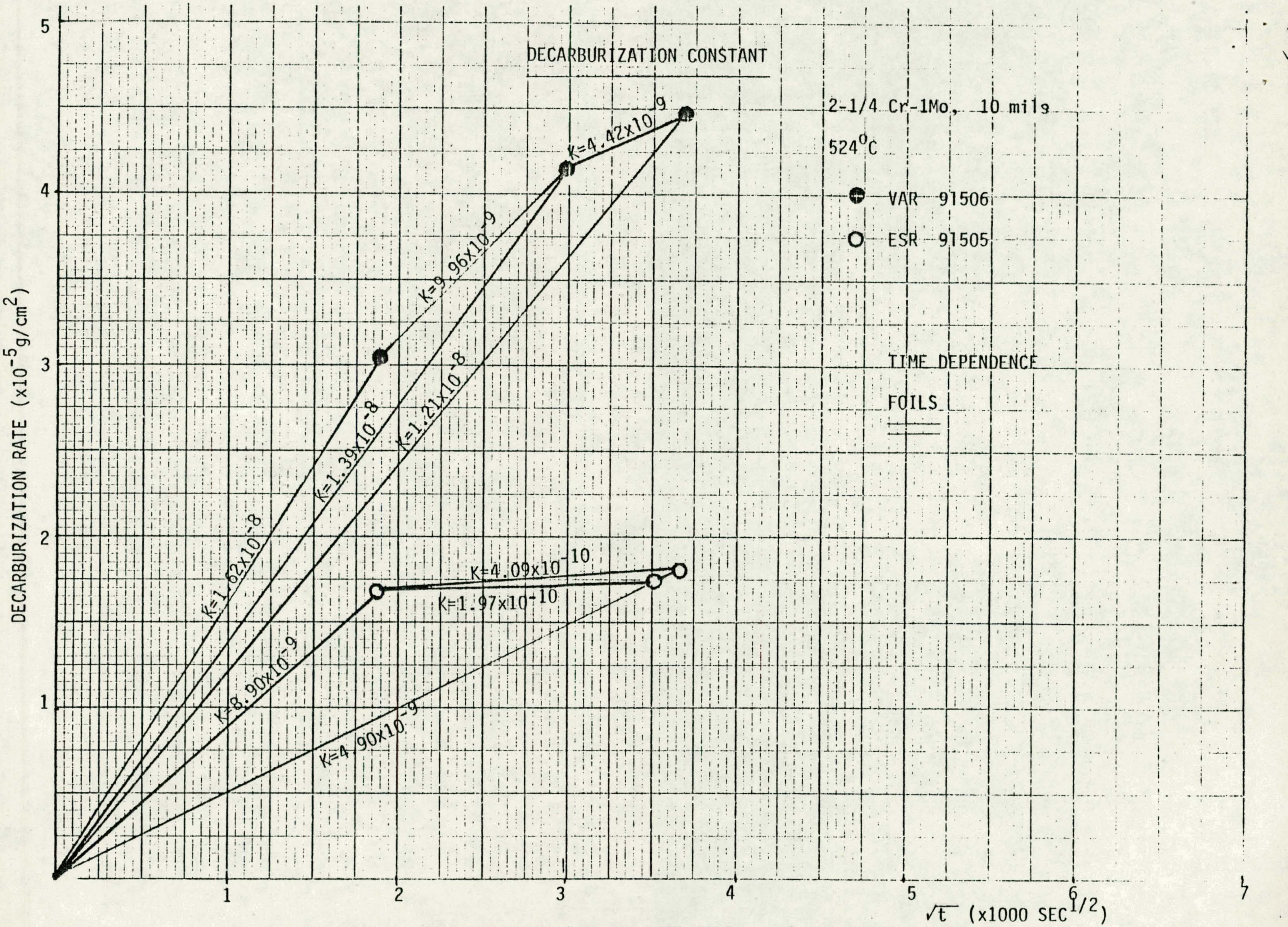
TEMPERATURE (°C)
550
500
450
400
350
VAR 91506 FOIL 10 mils
ESR 91505 FOIL 10 mils
VAR 91506 TUBE 113 mils
ESR 91505 TUBE 113 mils
3478 hrs.
7269.5 hrs.
3478 hrs.
7269.5 hrs.
3478 hrs.
7269.5 hrs.
3478 hrs.
7269.5 hrs.
3791.5 hrs.
Upper Limit Curve
3791.5 hrs.
DECARBURIZATION RATE CONSTANT K (g/CM²-SEC^1/2)
10^-6
10^-7
10^-8
10^-9
1.2
1.3
1.4
1.5
1.6
RECIPROCAL TEMPERATURE, 1000/T (K^-1)



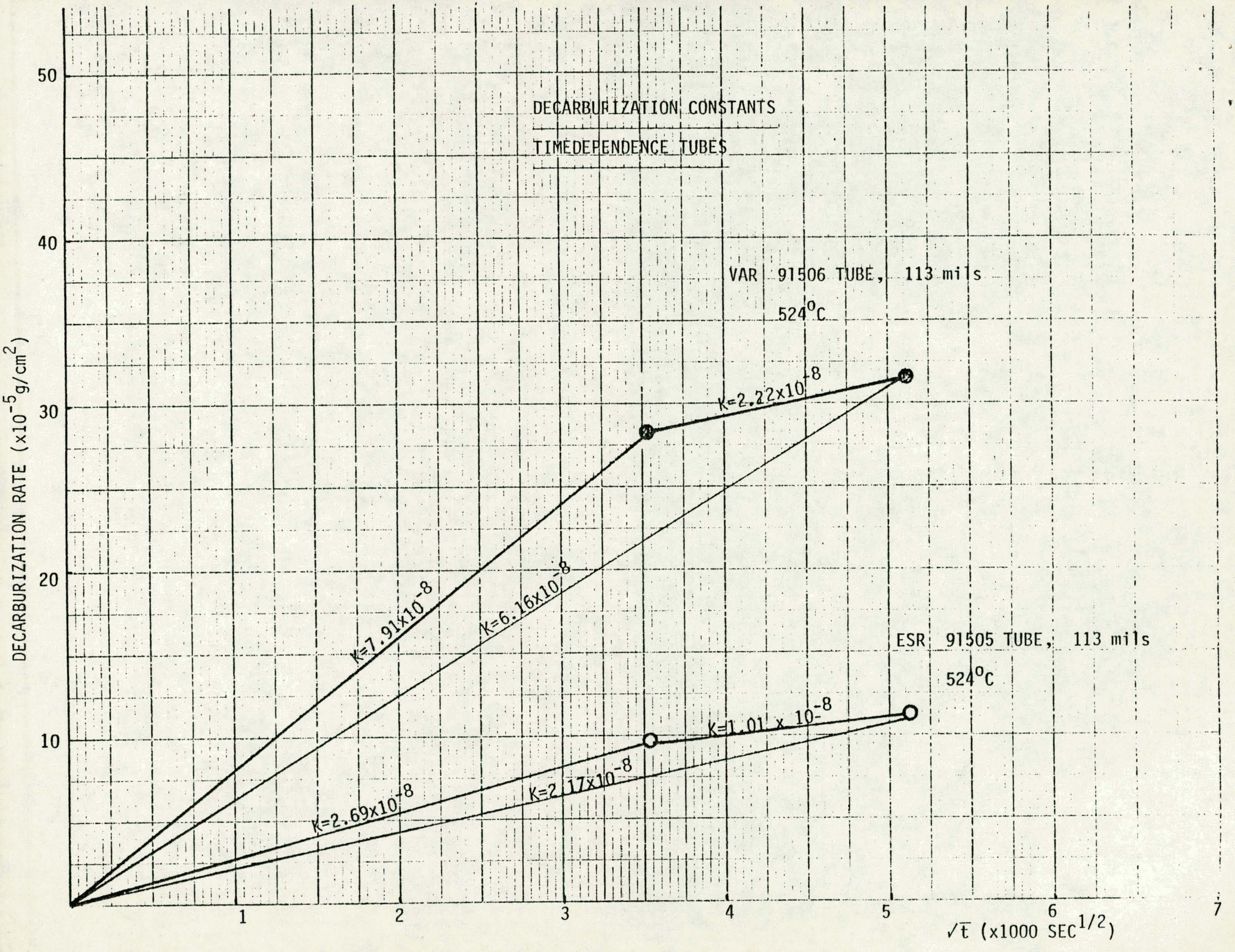
US - JAPAN DATA COMPARISON
(K)
TEMPERATURE (°C)
700
650
600
550
500
450
400
350
10^-6
10^-7
10^-8
10^-9
K (g/cm^2-SEC^1/2)
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1000/T (K^-1)
5 Kcal/mol
24 Kcal/mol
UPPER LIMIT CURVE
IHI
Anneal
VAR FOIL 10 mils
VAR TUBE 113 mils
ESR FOIL 10 mils
ESR TUBE 113 mils
Anneal (F + P + (B))
N + 1h Temper (100% TB)
N + 10h Temper (100% TB)
N + 1h Temper (F + TB)
N + 10h Temper (F + TB)
N (F + B)
SUMITOMO
by pot

US - JAPAN DATA COMPARISON (K^1)





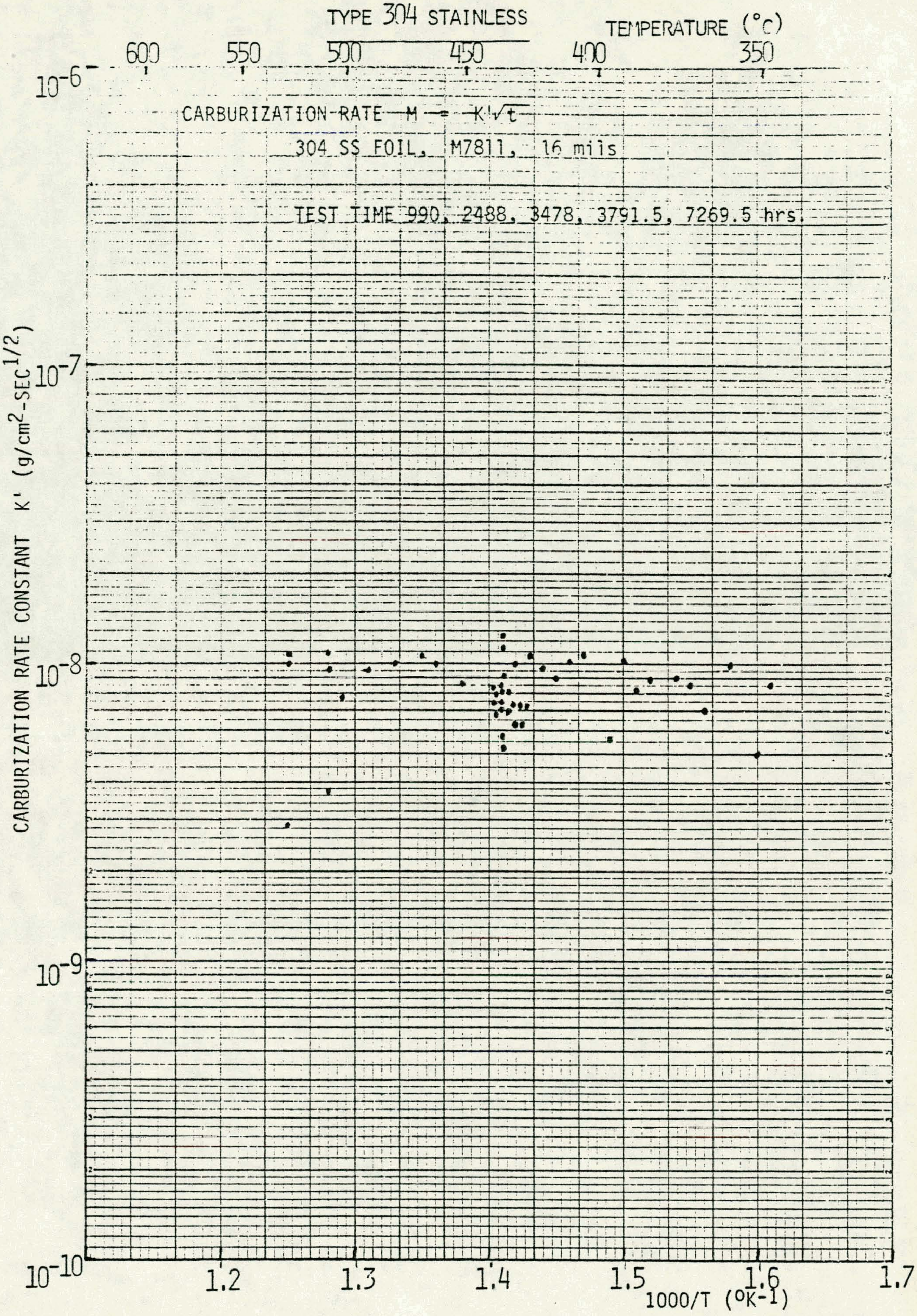
RELATION BETWEEN DECARBURIZATION RATE AND ROOT TIME FOR 2-1/4 Cr-1Mo at 524°C



DECARBURIZATION CONSTANTS
TIMEDEPENDENCE TUBES
VAR 91506 TUBE, 113 mils
524°C
ESR 91505 TUBE, 113 mils
524°C
K=2.22x10-8
K=7.91x10-8
K=6.16x10-8
K=1.01 x 10-8
K=2.17x10-8
K=2.69x10-8
DECARBURIZATION RATE (x10-5g/cm2)
50
40
30
20
10
1
2
3
4
5
6
7
√t (x1000 SEC1/2)

CARBURIZATION RATES

TYPE 304 STAINLESS



RELATION BETWEEN CARBURIZATION RATE CONSTANT AND TEMPERATURE FOR 304 SS