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THE INFLUENCE OF TEMPERATURE AND ALLOYING ELEMENTS
ON THE SOLUBILITY OF GRAPHITE IN LIQUID COBALT

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INTRODUCTION

Studies of the effects of temperature and alloying additions on the solubility of graphite in liquid metals have been limited essentially to iron systems until recently. During the last decade, however, two investigations have been made on the cobalt-carbon system. Turkdogan, Hancock, and Herlitz⁽¹⁾ studied the effect of temperature on the solubility of graphite in cobalt, as did Kojima and Sano,⁽²⁾ who also examined the influence of the alloying elements: chromium, manganese, molybdenum, nickel, and vanadium on graphite solubility in cobalt. An investigation similar to the present study has been carried on independently and concurrently, and has just been published by Schenck, et al.⁽³⁾

Of considerable interest today are techniques for predicting in a mixture, the effect of one component on the thermodynamic properties of other components, and many metallurgical ternary systems have been studied envisioning this goal of perfecting predictive techniques. Carl Wagner⁽⁴⁾ originated the interaction parameter concept, which presents ternary data in a form which is simple, and yet provides the greatest amount of useful information for estimating thermodynamic interactions between components in multi-component systems. Ohtani and Gokcen⁽⁵⁾ and Neumann, et al.⁽⁶⁾ have utilized the interaction parameter concept in attempting to correlate the position of alloying elements in the Periodic Table with their influence on carbon solubility in liquid iron alloys.

The interaction parameter comes from a Taylor series expansion for the logarithm of the activity coefficient:

$$\begin{aligned} \ln \gamma_i = & \ln \gamma_i^{\circ} + [X_i \left(\frac{\partial \ln \gamma_i}{\partial X_i} \right)_{\substack{X_i=0 \\ X_j=0}} + X_j \left(\frac{\partial \ln \gamma_i}{\partial X_j} \right)_{\substack{X_i=0 \\ X_j=0}} + \dots] \\ & + \left[\frac{1}{2} X_i^2 \left(\frac{\partial^2 \ln \gamma_i}{\partial X_i^2} \right)_{\substack{X_i=0 \\ X_j=0}} + X_i X_j \left(\frac{\partial^2 \ln \gamma_i}{\partial X_i \partial X_j} \right)_{\substack{X_i=0 \\ X_j=0}} + \dots \right] + \end{aligned} \quad (1)$$

where $X_i, X_j \dots$ are the mole fractions of dilute solutes in an alloy. If all terms except those of first order are neglected, the expression becomes linear with respect to the mole fractions of the solutes present in the alloy. If the interaction parameter is then defined as:

$$\epsilon_i^j = \left(\frac{\partial \ln \gamma_i}{\partial X_j} \right)_{\substack{X_i=0 \\ X_j=0}} \quad (2)$$

the expression for the logarithm of the activity coefficient becomes:

$$\ln \gamma_i = \ln \gamma_i^{\circ} + X_i \epsilon_i^i + X_j \epsilon_i^j + \dots \quad (3)$$

The interaction parameter ϵ_i^j represents the effect of component j on the activity coefficient of component i when both are very dilute. By definition, these parameters are calculated at infinite dilution and are applicable only in dilute solutions. However, carbon solubility studies are often performed by melting metals or their alloys in graphite crucibles and allowing the system to reach equilibrium. Such a system is not a constant dilute carbon concentration, but at constant carbon activity with the carbon at saturation in the melt. The relationship between these two situations has been developed by Fuwa and Chipman⁽⁷⁾ and can be written:

$$\left(\frac{\partial \ln \gamma_C}{\partial X_j} \right)_{X_C} = \left[1 + \left(\frac{\partial \ln \gamma_C}{\partial \ln X_C} \right)_{X_j=0} \right] \left(\frac{\partial \ln \gamma_C}{\partial X_j} \right)_{a_C} \quad (4)$$

This can be expressed as:

$$\epsilon_C^j = kE_C^j \quad (5)$$

where E_C^j is defined as $\left(\frac{\partial \ln \gamma_C}{\partial X_j}\right)_{a_C}$ and k is a constant for the base metal under consideration and is equal to $\left[1 + \left(\frac{\partial \ln \gamma_C}{\partial \ln X_C}\right)_{X_j=0}\right]$. In the cobalt-carbon system, the variation in carbon activity with concentration has not been studied, and therefore k is not available for this system. In studying the influence of alloying additions on carbon solubility in liquid cobalt, both Kojima and Sano⁽²⁾ and Schenck, et al.⁽³⁾ worked with a constant activity system and presented their results in the form of an interaction parameter of the type E_C^j .

EXPERIMENTAL PROCEDURE

A resistance furnace with an impervious mullite furnace tube was used for the solubility studies. The tube was sealed at both ends with an o-ring and head arrangement to provide an airtight system. Oxygen and moisture were removed from commercial argon before using it as an atmosphere in the system. The system was purged with argon before heating the sample and then a positive pressure of about ten millimeters of mercury was maintained with argon in the system during the experimental run.

The cobalt and cobalt alloys were held in a graphite crucible as shown in Figure 1. A hole in the bottom of the crucible was provided for a thermocouple temperature measurement. The temperature of the bath was maintained to within $\pm 2^{\circ}\text{C}$ during equilibration. A graphite lid was used on the crucible to minimize thermal gradients at the melt. A three-eighths inch diameter rod, flattened at one end to form a paddle, was used to intermittently stir the melt and increase the rate of approach to equilibrium. A seven millimeter (OD) vycor tube with a suction bulb was used for sampling. A roll of copper gauze was inserted in the vycor tube to serve as a chill and to limit the size of sample taken.

The cobalt used in this program was 99.5+% pure. The graphite and alloying elements used were all at least 99.9+% pure.

The experimental method involved melting approximately 200 grams of cobalt and ten grams of alloying element in the graphite crucible. After reaching the desired temperature (all the studies on alloy compositions were conducted at 1375°C) the melt was maintained there for 90

minutes with intermittent manual stirring. It had been previously determined that equilibrium was reached in the cobalt-carbon system in less than one hour under these conditions. At the end of this equilibration time, approximately ten grams was withdrawn in the vycor sampling tube and quenched. Another known quantity of alloying element was then added to the melt to change its composition. Again the melt was maintained at temperature for 90 minutes to attain equilibrium at this new alloy composition. This procedure was continued until the desired number of cobalt - j compositions were studied.

The charge materials and all samples that were removed were carefully weighed so a complete mass balance could be made to determine the alloy composition for each sample. This procedure was followed for each alloying element studied. By making complete chemical analyses on several of the samples, it was possible to verify the validity of this mass balance technique for obtaining alloying element compositions.

RESULTS

The solubility of graphite in cobalt as a function of temperature is shown in Figure 2. Also shown are the data for this system given by Turkdogan, et al.⁽¹⁾ and Kojima and Sano;⁽²⁾ the solubility curve without the data points is given from the work of Schenck, et al.⁽³⁾ The agreement between these investigations is good. By thermal analysis the cobalt-carbon eutectic was experimentally determined to be 1320°C, while both Turkdogan and Kojima reported the eutectic at 1319°C. A regression analysis was performed on the experimental data which yielded the temperature dependence of the graphite solubility in liquid cobalt as:

$$\text{Log } X_C = - \frac{1110}{T^{\circ}\text{K}} - 0.240 \quad (6)$$

This compares with the equations found for the relationship by other investigators:

$$\text{Turkdogan:}^{(1)} \quad \text{Log } X_C = - \frac{1050}{T} - 0.265$$

$$\text{Schenck:}^{(3)} \quad \text{Log } X_C = - \frac{1094}{T} - 0.245$$

Figure 3 shows the results of the experimental study of the effect of alloying elements on the solubility of graphite in cobalt. From the plots of Figure 3 the interaction parameters E_C^j were calculated and the results tabulated in Table I, along with the findings of the other investigators. In Figure 5, these same parameters were then plotted as a function of the atomic number of the alloying element j , showing the periodicity of their relationship.

CONCLUSIONS

1. The solubility of graphite in liquid cobalt was studied as a function of temperature. The temperature dependence of graphite solubility in liquid cobalt is given by the relationship:

$$\text{Log } X_C = - \frac{1110}{T^{\circ}\text{K}} - 0.240$$

2. The solubility of graphite in liquid cobalt was observed to be decreased by additions of silicon, copper, and nickel and to be increased by additions of tantalum, molybdenum, vanadium, chromium, tungsten, columbium, manganese, and iron.
3. The interaction parameters E_C^j were observed to vary systematically with the atomic number of the added alloying element j.

ACKNOWLEDGEMENT

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TABLE I

INTERACTION PARAMETER E_C^j FOR COBALT-CARBON SOLUTIONS

Alloy	This Study	Kojima and Sano ⁽²⁾	Schenck et al. ⁽³⁾
Al			+2.38
As			+4.81
Au			+2.03
B			+3.67
Cb	-1.83		-
Ce			-6.00
Cr	-2.20	-2.42	-2.94
Cu	+1.50		+1.70
Fe	-0.60		-0.23
Ge			+2.12
Mn	-0.77	-1.31	-0.68
Mo	-2.80	-2.42	-2.62
Ni	+0.36	+0.41	+0.22
P			+3.94
Pd			+1.01
Rh			0
Ru			-1.02
S			+4.75
Si	+3.90		+3.16
Sn			+3.50
Ta	-3.00		-3.68
Te			+5.63
U			-4.77
V	-2.35	-3.13	-4.00
W	-2.15		-1.70

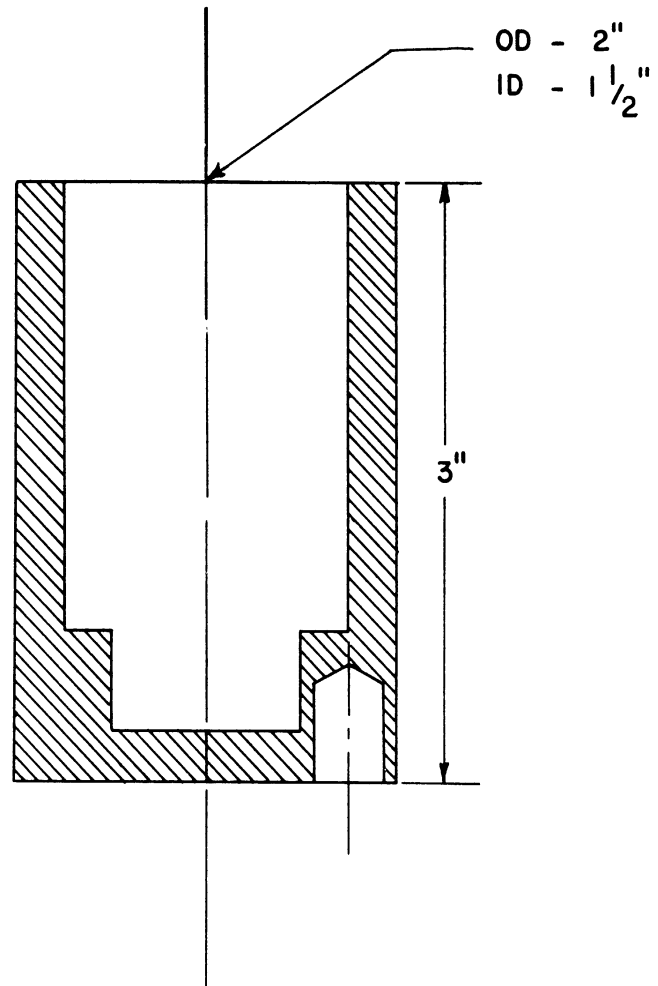


Figure 1. Graphite Crucible Showing Well
for Thermocouple Protection Tube.

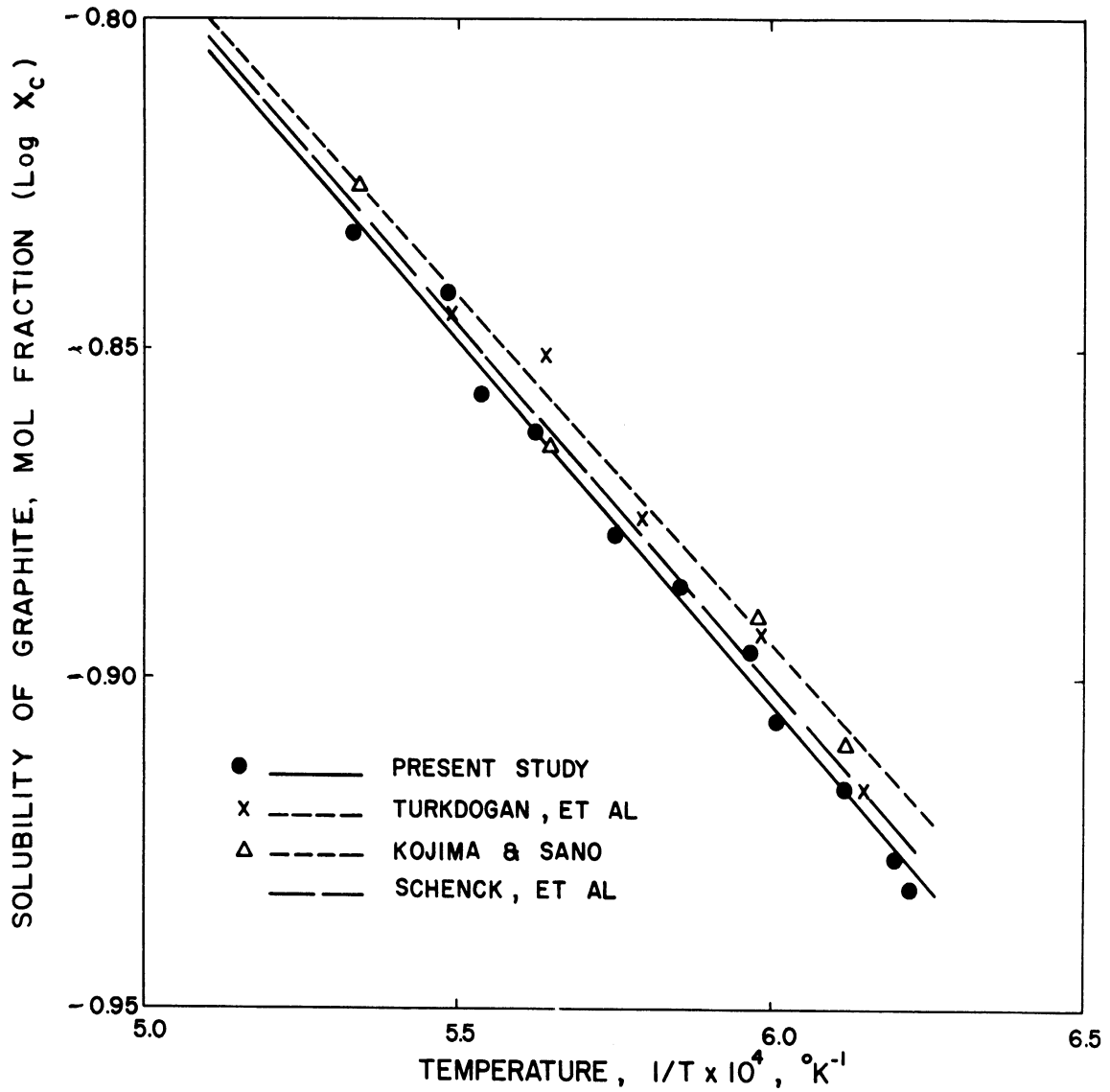


Figure 2. Solubility of Graphite in Cobalt as a Function of Temperature.

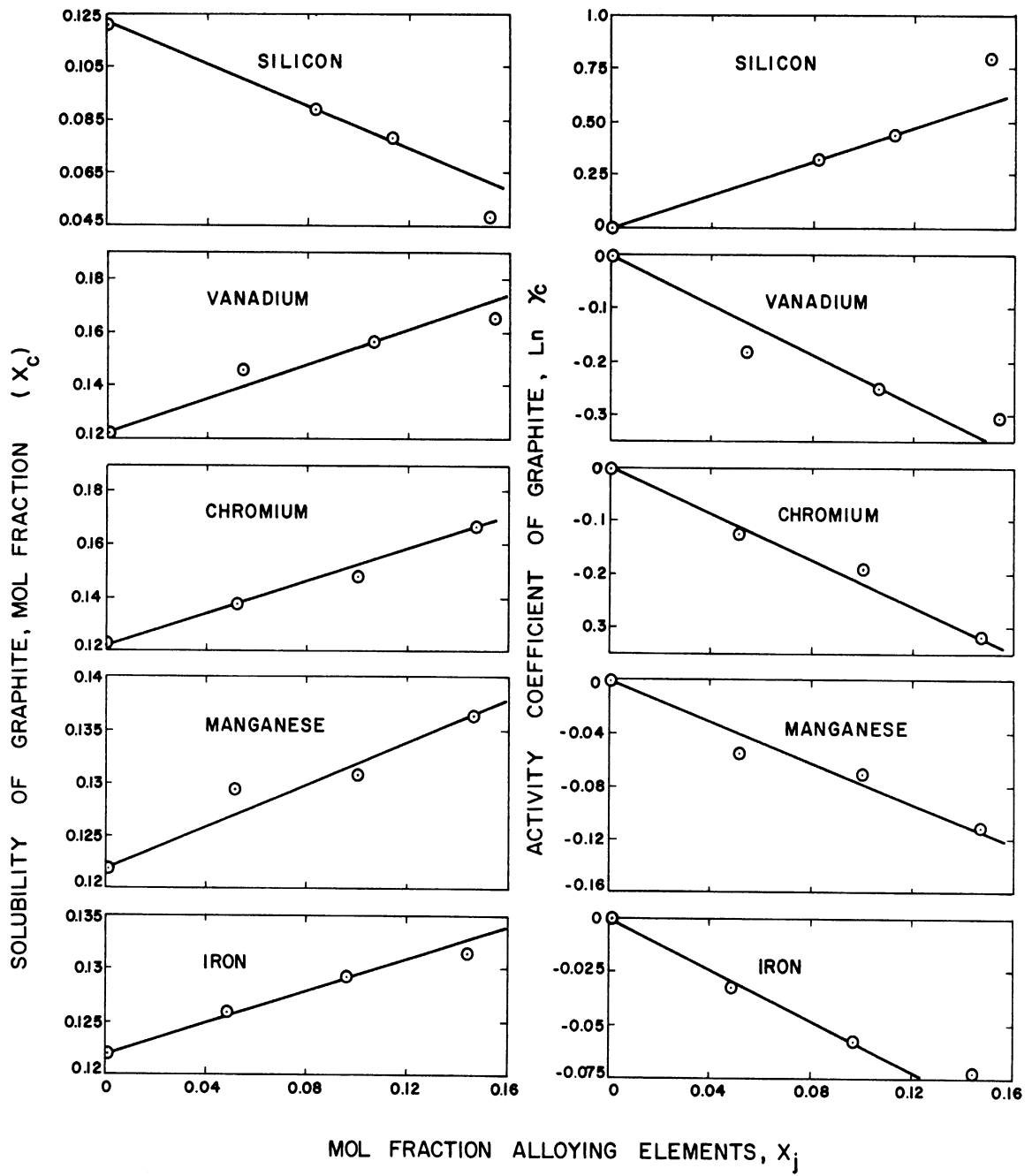


Figure 3. Effect of Alloying Elements on the Solubility and Activity Coefficient of Graphite in Cobalt at 1375°C.

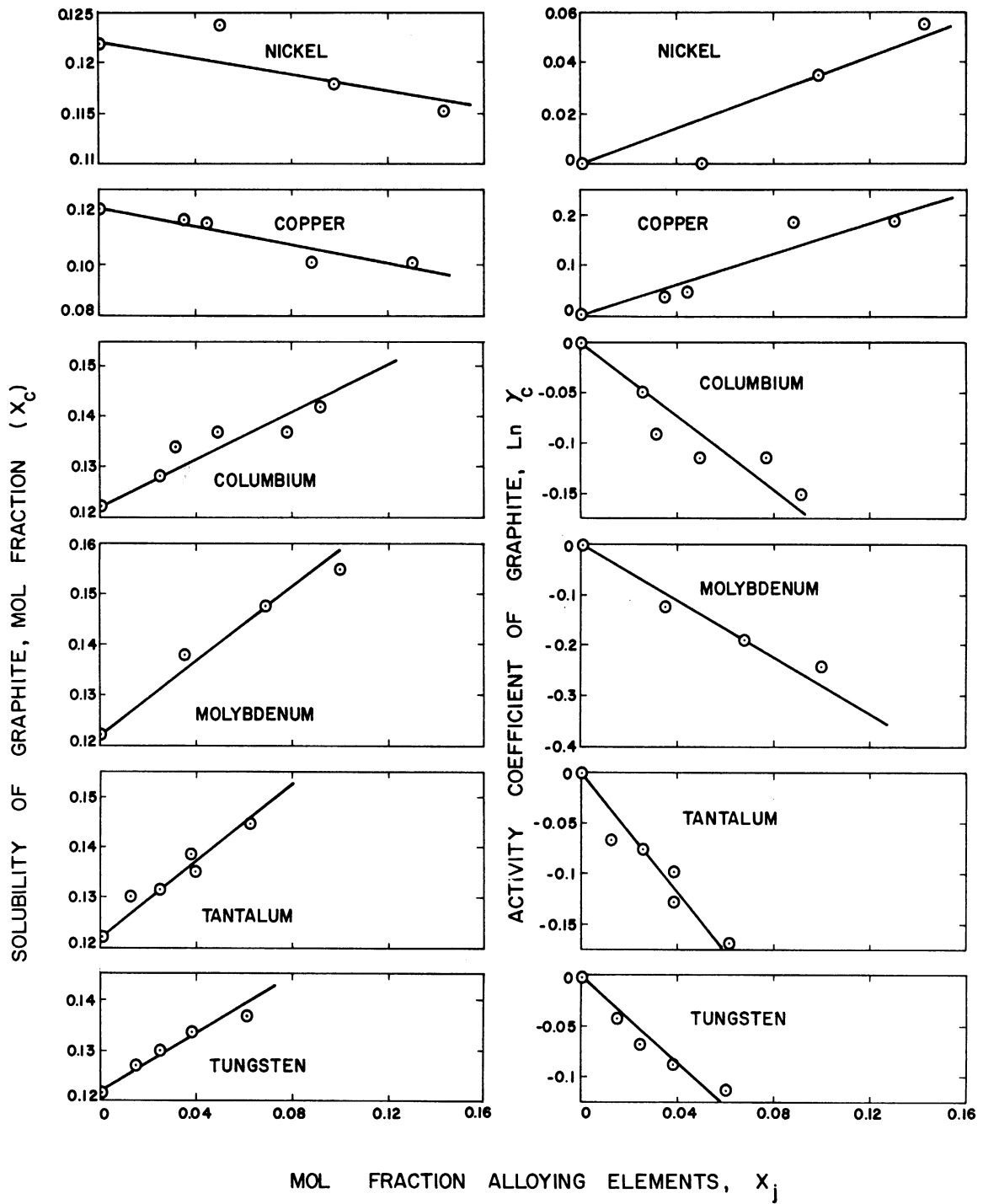


Figure 3 (Cont'd)

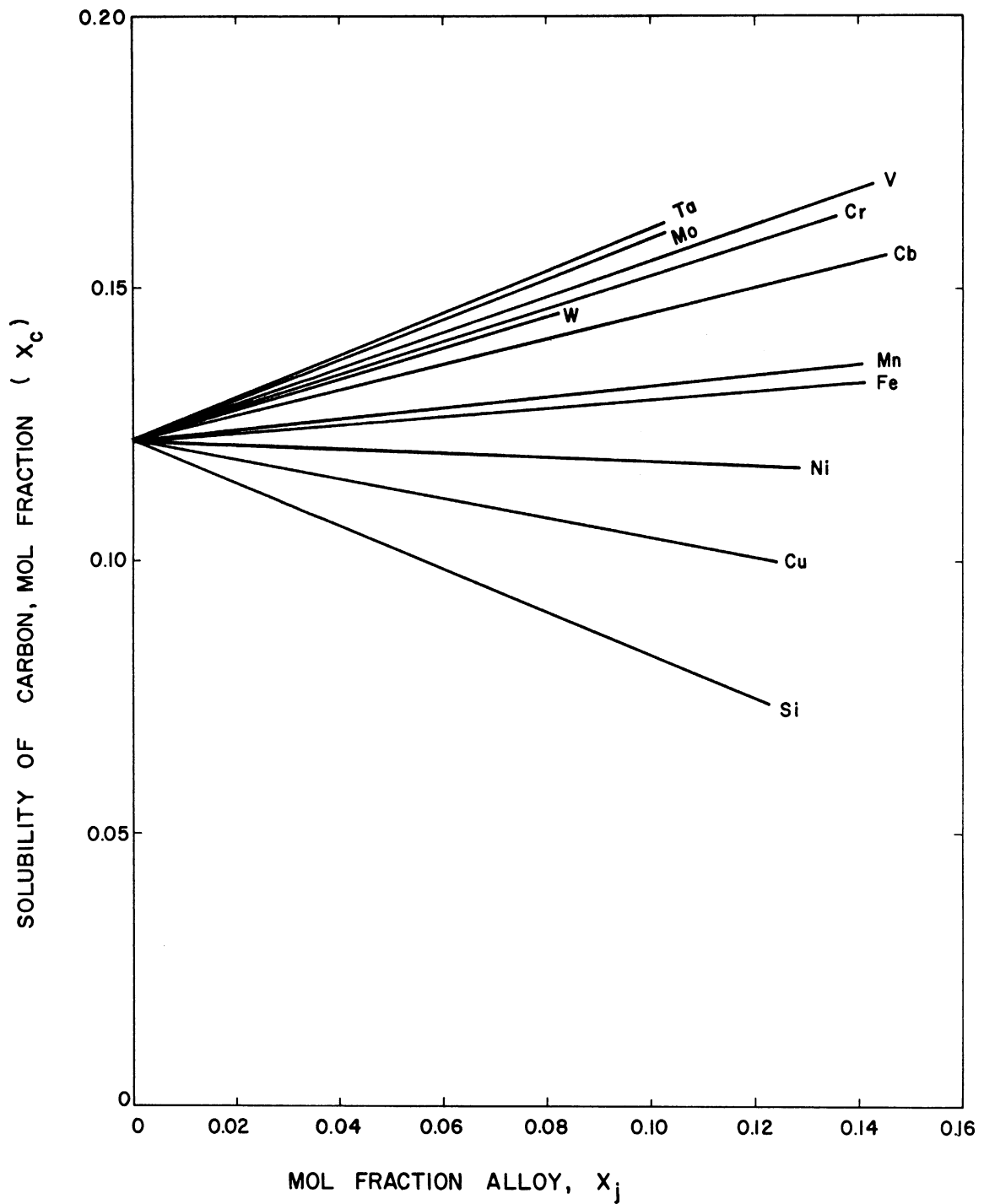


Figure 4. Effect of Alloying Elements on the Solubility of Graphite in Cobalt at 1375°C.

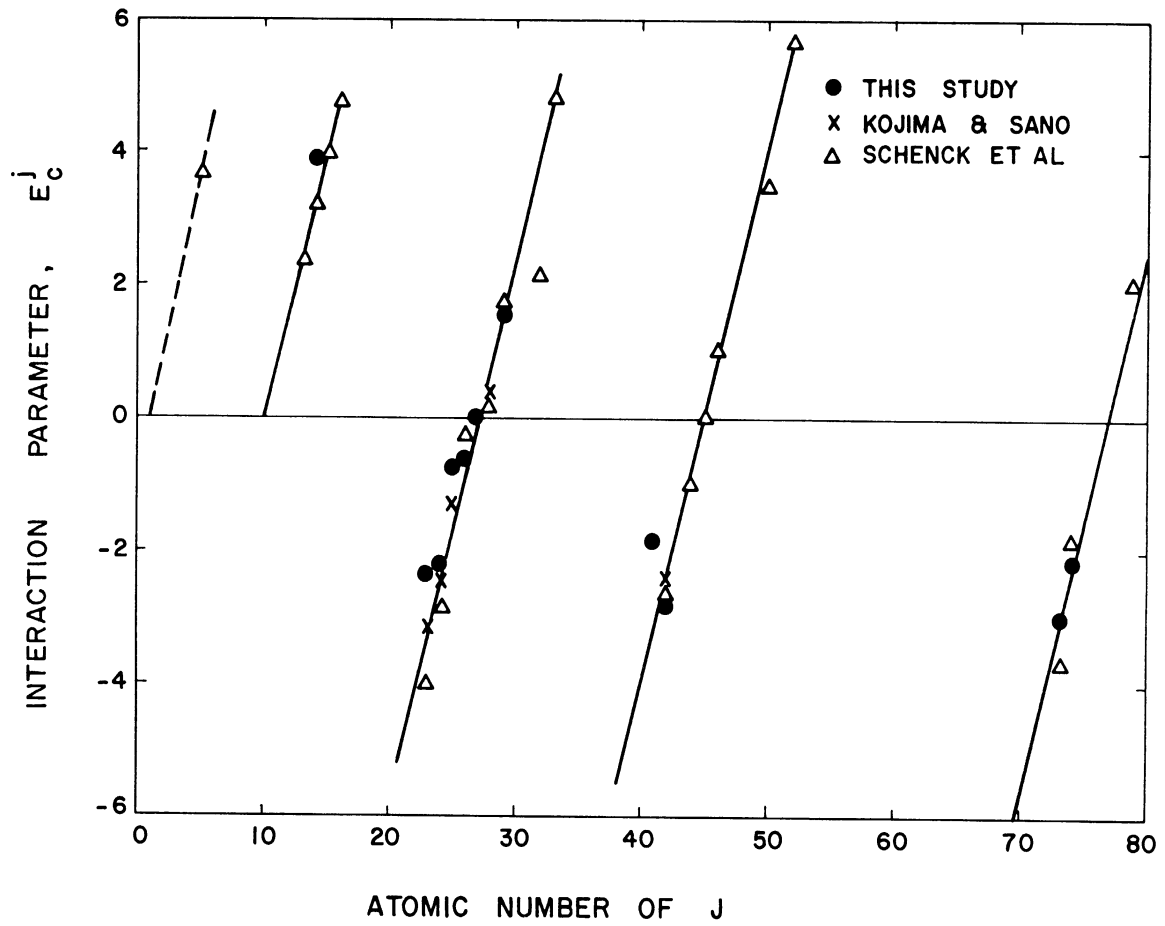


Figure 5. Correlation between Atomic Number of Alloying Element and Its Effect on the Activity Coefficient of Graphite in Cobalt.

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