A Study of the Reaction Kinetics for the Formation of Rare Earth–Transition Metal Laves Compounds

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The kinetics of the reaction $A_{(s)} + 2B_{(s)} = AB_{2(s)}$ was studied by differential thermal analysis. The A component was Pr, Gd, Dy or Er, the B was Fe, Co, or Ni and the resulting AB_2 compound was a $MgCu_2$ Laves intermetallic compound. A generalized search method to determine the reaction mechanism was developed and applied to the above reactions. The reactions were found to be diffusion controlled and the kinetics best described by the Valensi-Carter equation.

INTERMETALLIC compounds containing the rare earth metals are becoming the subjects of investigation due to their increasing industrial importance. Although the rare earths are prolific formers of intermetallic compounds the literature[1] indicates that their importance to the steel industry will be as desulfurizing and deoxidizing agents. Many of the intermetallic compounds of the rare earths with cobalt and nickel are used as permanent magnets. For example, permanent magnets based on $SmCo_5$ are the most powerful magnets known. Although a great deal of information on the magnetic properties of the rare earth intermetallics is available,[2] very little is known regarding their thermodynamic and kinetic characteristics. This information will be useful in understanding and predicting the behavior of rare earth metals in alloys and permanent magnets.

The reactions of rare earth metals with iron, cobalt or nickel take place entirely in the solid state. Although the kinetics of solid state reactions is a widely researched area, most of the work has been done in the field of ceramics. Differential thermal analysis (DTA)[3-8] has been used by many to study the kinetics of solid state reactions. In a typical differential thermal analysis experiment a reactive mixture and a nonreactive reference are heated at a uniform rate until the reactive mixture has completely reacted. During that time changes in the temperature of the reactive mixture relative to the temperature of the nonreactive reference are measured. The area under the change in temperature *vs* time curve is a measure of the heat of reaction. Different methods have been suggested and used to deduce kinetic data from DTA thermograms. One of the fundamental difficulties, however, is that the reaction occurs under nonisothermal conditions. Kissinger[3,4] used the variation in the peak temperature with the heating rate to determine the activation energy. The order of reaction was obtained from the shape of the thermogram. The first systematic method involving a trial and error procedure was developed by Borchardt and Daniels.[5] The trial and error procedure involved in the above method was eliminated by Freeman and Carroll.[6] Simmons and Wendlandt[7] have suggested some methods for treating nonisothermal kinetics. In this work one of the methods suggested by the above was used to develop a generalized method to determine the reaction mechanism most consistent with the experimental data.

EXPERIMENTAL

The kinetics for the formation of several Laves intermetallic compounds by a direct reaction of the elemental metals was studied. All compounds studied were of the composition AB_2 where the A component was a lanthanide element (Pr, Gd, Dy or Er) and the B component a transition metal (Fe, Co or Ni). The crystal structure of all the compounds studied was identical, *i.e.* $MgCu_2$ type. The compound $PrFe_2$ is nonexistent. Fine elemental powders of both components were mixed in stoichiometric proportion, sealed under vacuum and subjected to differential thermal analysis (DTA).

A differential thermal analysis calorimeter capable of operating under a vacuum of 10^{-6} Torr up to a temperature of 1500 K was constructed. A description of the calorimeter has been given elsewhere.[8] The lanthanide and transition metal elements were obtained from the Ventron Corp. and were 99.9 pct and 99+ pct pure, respectively. The particle size of the lanthanides was 2.5×10^{-4} meters (−60 mesh) and that of the transition metals was 4.4×10^{-5} meters (−325 mesh). All metal powders were weighed and mixed in a dry box which was maintained under a nitrogen atmosphere. Quartz vials (see Ref. 8) were used as containers for the reactant mixtures. The vial containing the reactant mixture was sealed off under vacuum and placed in the sample block of the DTA. Sealing under vacuum was done to restrict the evaporation, if any, to the quartz vial, and to prevent any oxidation during the calorimetric experiment. Tungsten powder sealed in an identical quartz vial was used as the DTA reference. Once loaded with sample and reference the calorimeter was sealed, evacuated and the temperature increased at a uniform rate of 8 K/min. In all cases the reactions were found to be exothermic. In no case was a reaction with quartz observed.

The DTA calorimeter was calibrated utilizing materials with known heats of fusion (see Ref. 8). The following equation was used to evaluate the heat

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evolved up to any given time (t).

$$H = \int_0^t ad\ \frac{d\Delta T}{dt} + \int_0^t bd(\Delta T) + \int_0^t h\,(\Delta T)dT \qquad [1]$$

H is the heat evolved up to time t, ΔT is the differential temperature, h, the heat transfer coefficient as determined from the calibration curve, a and b are functions of the heat capacities and weights of the sample and reference. The terms a, b and h are functions of temperature. Integration of the above equation was done numerically on an IBM 370 computer.

The rate of heat evolution and the rate of reaction are related as follows:

$$\frac{dH}{dt} = \Delta H_T\ \frac{dx}{dt} \qquad [2]$$

where x is the fractional conversion and ΔH_T is the heat of reaction at temperature T.

When unknown, the heat capacities of the intermetallic compounds were calculated utilizing the Kopp-Newmann rule.[9] When this procedure is used the heat of reaction will be independent of temperature. For metallic systems at temperatures where the Law of Dulong and Petit holds, the heat of reaction is nearly independent of temperature over a small temperature increment. For this work, the increment is the temperature range over which the reaction takes place and was found to be 25°C on the average.

Eq. [2] can be integrated and combined with Eq. [1]. The total heat evolved during reaction was measured and used to calculate the fractional conversion as a function of time.

Only those experiments in which the reaction went to completion were considered valid for analysis. A reaction was considered complete if no trace of the reactant elements could be detected by X-ray diffraction.

METHOD OF CALCULATION

It was found that all the reactions investigated took place while the reactants and products were solid. Many reaction mechanisms and rate equations to describe solid state reactions in powdered compacts have been proposed.[10] The rate equations can be classified under three categories based on the rate determining step in the reaction mechanism. In the first, product growth is controlled by diffusion of reactants through a continuous product layer. In the second product growth is controlled by nuclei growth and in the third by phase boundary reactions.

The procedure employed for kinetic calculations is as follows. The general form of a rate equation was written as:

$$\frac{dx}{dt} = kf(x) \qquad [3]$$

The integrand of the above equation was then written as:

$$g\,(x) = kt \qquad [4]$$

where $g\,(x)$ and $f(x)$ are certain functions of x; the form of which is determined by the reaction mechanism. Knowing $g\,(x)$, $f(x)$ can be derived from it and *vice versa*. It was assumed that the variation of the rate constant with temperature followed the Arrhenius law.

$$k = A \exp\,(-E/\mathrm{R}T) \qquad [5]$$

The values of the frequency factor, A, and activation energy, E, are independent of temperature. In case of diffusion in solids, the activation energy depends upon the concentration of diffusing species.[11,12] Thus the activation energy may be a function of reactant concentration.

A nonisothermal reaction was approximated as an isothermal reaction in many intervals of temperature.[7] A hypothetical experiment may be conducted in the following manner. First, the temperature is maintained at T_0 from time 0 to Δt, at time Δt it is instantaneously changed to T_1. The sample is then held at temperature T_1 until time $2\Delta t$, at which time the temperature is instantaneously changed to T_2. The process is continued until the reaction is complete. For any isothermal time interval, Eq. [4] can be written as:

$$g\,(x_{i+1}) - g\,(x_i) = \mathrm{A} \exp\,(-E/\mathrm{R}Ti)\,\Delta t \qquad [6]$$

The left hand side of the above equation can be evaluated from experimental results. The activation energy was assumed to be constant over the short time interval, Δt, and a function of x. The activation energy for each time interval can then be calculated from Eq. [6].

The fractional conversion, x as a function of time was evaluated from Eq. [2]. The values of $g(x)$ were evaluated, assuming a certain reaction mechanism and kinetic equation. Table I gives a listing of the equations used. Values of the calculated rate constants were used in a plot of ln k *vs* $1/T$. This plot is not a single straight line, but rather a series of connected straight line segments, each with a slope of $-E/R$. The activation energy is a function of concentration, and this is the reason for the absence of a single straight line. Activation energies at different points were calculated. Knowing the relation between temperature and conversion, a plot of activation energy *vs* conversion was made. (Figs. 1 to 4).

Kinetic calculations were done for three types of mechanisms, *i.e.* diffusion, phase boundary and nuclei

Table I. Rate Equations for Solid State Reactions General Form: $kt = g(x)$

A. Diffusion Mechanism

Jander:
$k_j t = [1-(1-X)^{1/3}]^2$

Ginstling-Brounshtein:
$k_{gbt} t = \frac{2}{3} X - (1-X)^{2/3}$

Valensi-Carter:
$k_{vc} t\ \{Z - [1+(Z-1)X]^{2/3} - (Z-1)(1-X)^{2/3}\} \div (Z-1)$

Dunwald—Wagner:
$k_{dw} t = 6 \div \ln \pi^2 (1-X)$

Zurvalev-Lesokhin-Tempelman:
$k_{zlt} t = [(1-X)^{-1/3} - 1]^2$

Kroger-Ziegler:
$k_{kz}(\ln t) = [1-(1-X)^{1/3}]^2$

B. Nuclei Growth Mechanism

$\ln(1-X) = -kt^m$

C. Phase Boundry Mechanism

Sphere: $kt = 1-(1-X)^{1/3}$
Cylinder: $kt = 1-(1-X)^{1/2}$

growth. Results calculated from the equations based on phase boundary or nuclei growth controlled mechanisms, were unrealistic. Further, Arrhenius plots for these mechanisms showed a great deal of scatter indicating that the rate determining step was not phase boundary motion or nuclei growth.

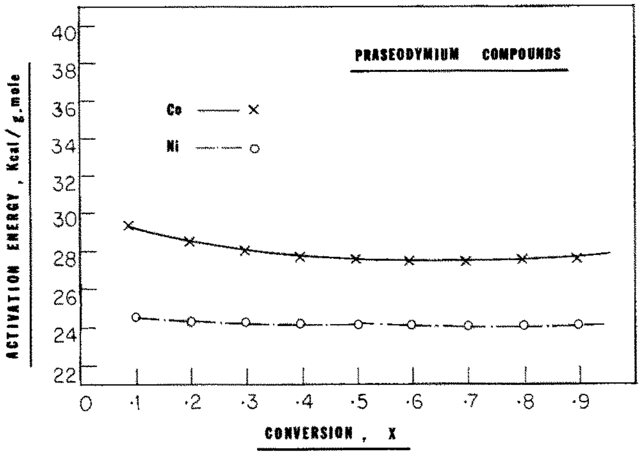

Fig. 1—Concentration dependence of activation energy for praseodymium compounds.

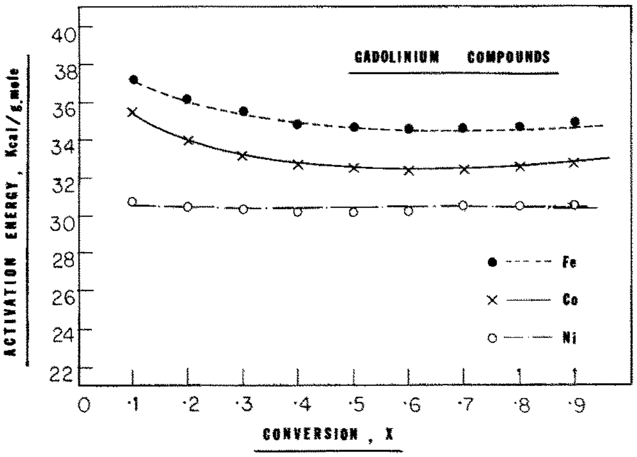

Fig. 2—Concentration dependence of activation energy for gadolinium compounds.

As an example, the results for the formation of Fe_2Dy are given below. For phase boundary controlled reaction and the spherical particle reacting from the surface inward, the activation energy is 255 kcal/mole. For a cylinder reacting from the surface inward, the activation energy is 273 kcal/g.mole. For the reaction controlled by nuclei growth, different values of *m* are assumed. The activation energies, assuming *m* as 0.5, 0.67, 1.0, 1.5, 2, are −10, 105, 220, 300 and 330 kcal/g.mole, respectively. The curve fit was found to be worse when low values of *m* were used.

Thus, it was concluded that the reactions studied were diffusion controlled. Kinetic data for the initial part of the reactions (up to about 10 pct conversion) often[13] do not fit a model very well. This, however, is reasonable since at low conversion, product does not completely separate the reactants from each other and both diffusion and phase boundary reactions are occurring.

A total of six equations for diffusion controlled reactions are given in Table I. The equations of Kroger-Ziegler assume that the diffusion coefficient or the rate constant varies inversely with time but otherwise is identical to the Jander equation. This assumption is more empirical then theoretical. The rate constant should be a function of only two variables namely, temperature and concentration. The dependence of temperature and concentration on time is empirical and will vary according to experimental conditions. The equations given by Dunwald-Wagner, and that of Zhurvalev, Lesokhin and Tempelman apply well for the early part of the reaction, *i.e.* up 50 pct conversion. Beyond 50 pct conversion the fit is poor. The Valensi-Carter equation has been derived by correcting the volume change deficiencies in the equations of Jander and Ginstling-Brounshtein. This last equation proved to be the most suitable for this study.

Kinetic calculations for all the reactions studied were made using the Valensi-Carter equation. This equation requires some additional data, *i.e.* the factor Z. The factor Z is a ratio of the volume of the product to the volumes of the reactants. To calculate Z, the densities of the intermetallic compounds were used. The densities of Co_2Dy, Co_2Gd, Ni_2Gd, and Co_2Pr are given by Savitaskii,[14] those of the other rare earth in-

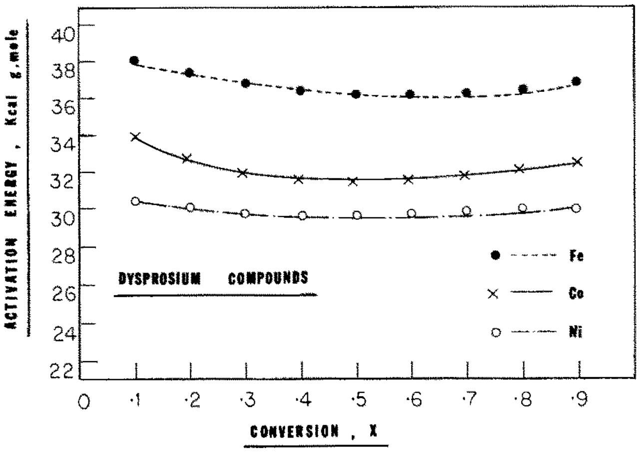

Fig. 3—Concentration dependence of activation energy for dysprosium compounds.

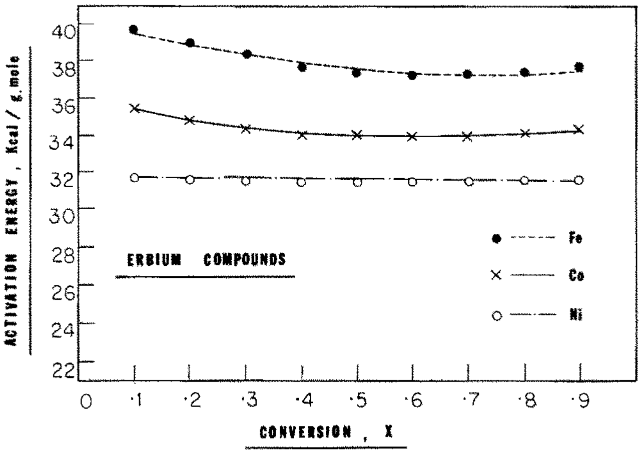

Fig. 4—Concentration dependence of activation energy for erbium compounds.

termetallics were calculated from crystallographic data.

All the rare earth intermetallics studied in this work are of the $MgCu_2$ type. They have a cubic lattice with 24 atoms or 8 molecules per unit cell. The volume of the cell is calculated from the lattice parameter. The lattice parameters, densities and values for the factor Z are given for all the intermetallics in Table II.

The rate constant k_{vc} is a function of particle size. The relation between k_{vc} and the standard form of the rate constant k is given by

$$k = r^2 k_{vc} \qquad [7]$$

where r is the radius of a reacting particle. For the final kinetic calculations Eqs. [5], [6], and [7] were combined. The actual calculations were carried out by computer. The heats of reaction, reaction temperatures, frequency factors, activation energies and rate constants at the respective reaction temperature are given in Table III. The reaction temperature is defined as a temperature at which the reaction begins.

DISCUSSION

The reactions of the rare earth elements with iron, cobalt and nickel took place at temperatures which were well below the melting points of both the components. The reactions are, therefore, entirely solid state. An intermetallic compound is stable with respect to competing neighboring phases if its free energy is lower (more negative) than that of a mixture of these phases. In a reaction involving solids only, the entropy change is small and for practical purposes, can be neglected. The negative change in enthalpy will then indicate the direction in a solid state reaction. Heats of reaction for the rare earth intermetallics formed from the elements are exothermic, which is in agreement with the above statement.

Table II. Lattice Parameters, Densities and the Factors Z

Compound	Lattice Parameter (Å)	Densities (g/cc)	Z
Co_2Pr	7.312	8.792	1.33
Ni_2Pr	7.285	8.875	1.32
Fe_2Gd	7.390	8.852	1.52
Co_2Gd	7.255	8.569	1.47
Ni_2Gd	7.202	9.766	1.46
Fe_2Dy	7.325	9.267	1.54
Co_2Dy	7.187	10.031	1.48
Ni_2Dy	7.155	10.150	1.46
Fe_2Er	7.273	9.631	1.54
Co_2Er	7.144	10.387	1.48
Ni_2Er	7.110	10.520	1.47

When a reactive mixture of solids is heated, and an exothermic reaction occurs, a point is reached at which the heat of reaction can no longer be dissipated to the surroundings under approximately isothermal conditions, and the temperature within the mass of the mixture rises appreciably. The consequent increase of rate further accelerates the heat evolution, and the reaction proceeds uncontrollably until it is eventually slowed down by the accumulation of solid products. The rate of reaction is further accelerated by the fine particle size of the reactants. A small particle size assures more surface area per unit mass and better mixing.

The reactions of rare earth intermetallics can be characterized by their reaction temperatures, *i.e.* the temperatures at which the reactions begin. Conversion prior to the reaction temperature was found to be negligibly small and for all practical purposes can be taken as zero. This was determined by heating the reactive mixture to a temperature which was a few degrees lower than the reaction temperature. It was then cooled and analyzed by X-ray diffraction. Diffraction patterns showed no trace of intermetallic compound. The reasons for a sudden outburst of the reaction at the reaction temperature could be numerous. A gaseous phase may act as a medium for the reaction, molten metal may be present at the time of reaction or the reasons may be strictly characteristic of the solid state. These reasons are discussed with respect to the reactions of rare earth intermetallics studied herein.

Vapor pressures of the rare earths as well as iron, cobalt, and nickel are very low at their corresponding reaction temperatures. For example, the vapor pressures of iron, cobalt or nickel at 1000 K are of the order of 10^{-10} Torr. The vapor pressures of praseodymium and gadolinium at the same temperature are of the order of 10^{-8} Torr. Vapor pressures of dysprosium and erbium at 1000 K are 10^{-5} and 10^{-6} Torr respectively. Even these last vapor pressure values are too low to influence or initiate the reaction. The

Table III. Results of Kinetic Analysis

Compound	Heat of Reaction (kcal/g mole)	Reaction Temperature (°C)	Frequency Factor (s^{-1})	Activation Energy (kcal/g mole)	Rate Constants at the Reaction Temperature ($\times 10^8\ s^{-1}$)
Co_2Pr	−3.1 ± 0.25	505 ± 3	1.53 ± 0.12	27.9 ± 0.2	2.5
Ni_2Pr	−6.0 ± 0.9	547 ± 4	0.58 ± 0.08	24.0 ± 0.1	25.6
Fe_2Gd	−2.5 ± 0.15	805 ± 5	1.58 ± 0.1	35.1 ± 0.3	13.4
Co_2Gd	−7.7 ± 1.2	727 ± 3	1.43 ± 0.15	33.0 ± 0.3	9.8
Ni_2Gd	−18.0 ± 2.0	658 ± 2	0.90 ± 0.05	30.4 ± 0.4	7.3
Fe_2Dy	−21.0 ± 1.9	818 ± 3	1.6 ± 0.1	36.75 ± 0.7	7.7
Co_2Dy	−6.5 ± 0.5	691 ± 10	0.9 ± 0.1	32.1 ± 0.6	5.3
Ni_2Dy	−27.6 ± 2.1	687 ± 7	0.67 ± 0.1	30.0 ± 0.5	11.0
Fe_2Er	−35.0 ± 3.8	865 ± 10	1.47 ± 0.1	38.1 ± 0.7	7.9
Co_2Er	−8.3 ± 1.1	750 ± 5	1.53 ± 0.2	34.25 ± 0.3	8.2
Ni_2Er	−35.3 ± 3.1	754 ± 4	0.42 ± 0.05	31.5 ± 0.05	9.2

Table IV. Conversion Factors to SI Units

To Convert from	to	Multiply by
cal/mole	J/mole	4.1840
atm	N/m^2	1.0132 × 10^5

quartz vials used as sample containers are evacuated prior to sealing. The vacuum at the time of sealing is at least 10^{-4} Torr. Thus, it is concluded that neither the metallic vapors nor the residual air influence or initiate the reaction.

A thin layer of molten metal at the interface of the reacting elements will accelerate the reaction due to greater mobility of the atoms in the liquid phase. The melting points of the reacting elements are much higher than their corresponding reaction temperatures. Also the presence of molten metal will change the final appearance of the product. Products were invariably found in the form of sintered powdered compacts and never in the form of solidified metals. The presence of a liquid has to be ruled out. Thus the factors which affect the reaction should be characteristic of the solid state.

Hedvall, who is one of the earliest to study solid state reactions, has given a general principle:[8] 'Every interference with the crystal lattice which sufficiently decreases its interior stability, increases the mobility of the units of the lattice, and therefore more or less stimulates the crystal to react with another crystal'. The factors which are likely to cause this interference could be an increase in temperature, a change in the crystal structure of one of the components, or the presence of foreign substances. The importance of these factors, with respect to the reactions of rare earth intermetallics is discussed below.

An increase in temperature causes an expansion of the crystal lattice and an increase in kinetic energy of the atoms. The probability that the atoms move outside their mutual fields of attraction increases. The reaction begins when the increase in kinetic energy of the atoms is sufficient to overcome the barrier of their mutual fields of attraction. The barrier is analogous to the activation energy term used in reaction kinetics. If the activation energy for the reaction is high, then the initiation temperature should also be high. To test this conclusion, reaction temperatures and activation energies were plotted. Fig. 5 is a plot of both against the atomic numbers of the rare earths and Fig. 6 is a plot against the atomic numbers of the transition elements. Two graphs are necessary for the comparison since an increase in kinetic energy of either of the reacting elements can initiate the reaction. The first observation is that the activation energy generally increases as the reaction temperature increases. One may conclude therefore that the kinetic energy increase caused by an increase in temperature is a determining factor for the initiation of the reactions studied herein. Further a similarity in the trends of reaction temperatures and activation energies is more pronounced in Fig. 5 than in Fig. 6. This leads to the conclusion that the increase in kinetic energy in the crystal lattices of the rare earth elements initiate the reaction. This conclusion is further supported if one considers the Tamman points of the elements involved in the present study. The Tamman point ($0.52T_{\text{melting}}$) is the temperature of the onset of mobility of lattice

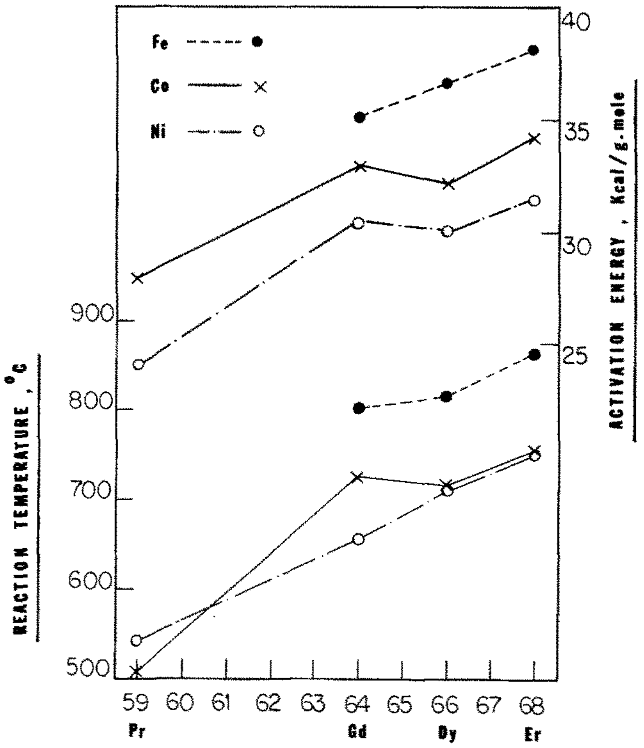

Fig. 5—Comparison of trends in activation energy and reaction temperature. Comparison is with respect to rare earth elements.

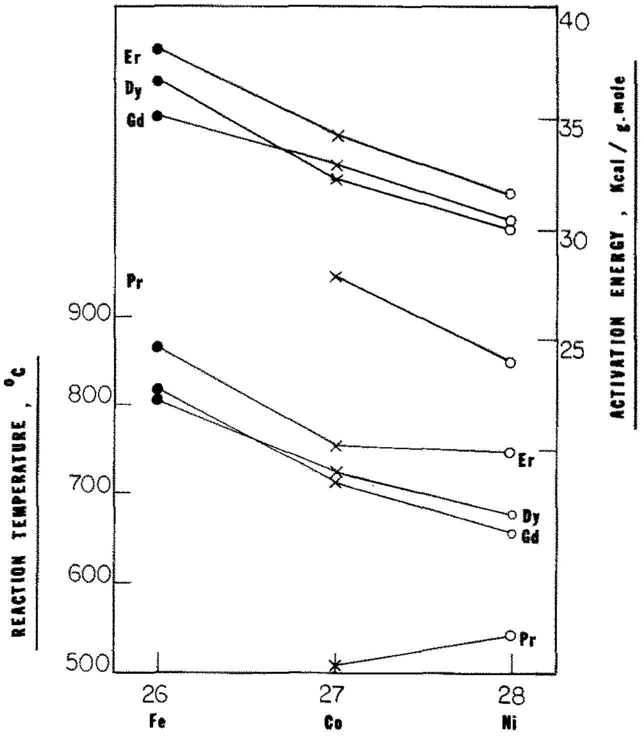

Fig. 6—Comparison of trends in activation energy and reaction temperature. Comparison is with respect to transition metal elements.

atoms or ions and is therefore an extremely important quantity in discussing the chemical reaction of solids. Since, with the exception of Erbium, the melting points of the rare earths is lower than that of the transition metals, one would expect that the chemical reaction is initiated by the diffusion of the rare earth member.

The second factor which can cause interference in the crystal lattice is the addition of small quantities of foreign constituents. Differences in the radii of atoms or ions, or the differences in the electrical charge between the original and the foreign particles will change the cohesion of the lattice. This will change the reactivity of the original solid. In the case of the reactions of rare earth intermetallics, all the elements used are of high purity (99.5 pct).

The third factor is a phase change for either of the reacting components. During a phase change, the particles have an abnormally great freedom of movement and abnormally great reactivity. The reaction temperatures for the reactions of rare earth intermetallics are nowhere near the phase transition temperatures of their constituent elements.

REFERENCES

1. N. Keppenhan and K. A. Gschneidner, Jr.: *Rare-Earth Metals in Steels,* Rare-Earth Information Center, Iowa State Univ., Ames, Iowa.
2. W. E. Wallace: *Progr. Solid State Chem.,* 1971, vol. 6, pp. 155-86.
3. H. E. Kissinger: *J. Res. Nat. Bur. Stand.,* 1956, vol. 57, pp. 217-24.
4. H. E. Kissinger: *Anal. Chem.,* 1957, vol. 29, pp. 170-206.
5. H. J. Borchardt and F. Daniels: *J. Amer. Chem. Soc.,* 1957, vol. 79, pp. 41-46. H. J. Borchardt: *J. Inorg. Nucl. Chem.,* 1960, vol. 12, pp. 252-54.
6. E. S. Freeman and B. Carroll: *J. Phys. Chem.,* 1958, vol. 62, pp. 394-97.
7. E. L. Simmons and W. W. Wendlandt: *Thermochimia Acta,* 1972, vol. 3, pp. 498-500.
8. D. M. Qualtieri and P. J. Ficalora: *High Temperature Science,* 1975, vol. 7, pp. 25-36.
9. O. Kubaschewski, E. Evans, and C. B. Alcock: *Metallurgical Thermochemistry,* Pergamon, New York, 1967.
10. S. F. Hulbert and J. J. Klawitter: *J. Amer. Ceram. Soc.,* 1967, vol. 50, p. 484.
11. P. J. Ficalora and G. W. Brindley: *J. Amer. Ceram. Soc.,* 1965, vol. 50, pp. 662-65.
12. W. Jost: *Diffusion in Solids, Liquids and Gases,* pp. 212-68, Academic Press, New York, 1960.
13. C. Wagner and K. Grünewald: *Z. Phys. Chem.,* 1938, vol. 40, p. 455.
14. E. M. Savitskii et al.: *Rare Earth Alloys*, Publishing House of the Academy of Sciences, USSR, Moscow, 1962. English translation by U.S. Atomic Energy Commission, No. AEC-tr-6151.
15. J. A. Hedvall: *Chem. Rev.,* 1934, vol. 15, pp. 139-68.