

References

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V_3Ga growth kinetics in vanadium/gallium-copper composites

V_3Ga is a β -W type superconducting compound with a high transition temperature, a high upper critical field and capable of carrying a high current density. Consequently, its production and properties have received considerable study during the past few years [1-5]. An important manufacturing process relies on the selective diffusion of gallium into vanadium from a gallium-copper alloy. In the process, a composite of vanadium and gallium-copper is fabricated as a tape or filamentary wire. The composite is mechanically deformed to the desired final size. A heat-treatment in the temperature range 575 to 800°C produces a V_3Ga layer at the interface between the vanadium and the gallium-copper. The purpose of the present paper is to show that a single equation can reproduce the growth rate of the V_3Ga layer at different reaction temperatures and for different compositions of the gallium-copper alloy.

The experimental data used for the basis of the analysis are taken from: Suenaga and Sampson [1] who used three vanadium rods embedded in a nominal 15 at. % gallium-copper matrix; Tachikawa *et al.* [2, 3] whose samples were strips of vanadium rolled in a 20 at. % gallium-copper sheath; Howe *et al.* [4] using a single vanadium filament in a 15.4 at. % gallium-copper sleeve; and Critchlow *et al.* [5] whose sample was a multifilamentary vanadium composite having a 14 at. % gallium-copper matrix. The growth rate data given by Suenaga and Sampson agree very closely to those of Critchlow *et al.*, and in the analysis it has been assumed that both sets of samples had the same composition, namely 14 at. % gallium.

In order to make comparisons between the superconducting properties of the V_3Ga layers, as produced by different workers, it has been customary to use data for a 1 μ m thickness. The reaction time, at different temperatures, required to produce this thickness is frequently reported. In the case of Tachikawa *et al.* [2], however, it was necessary to extrapolate the data given for the production of thicker layers to determine the time to grow a 1 μ m layer.

The basic equations governing the rate of growth of a diffusion layer are:

$$x^2 = kt \quad (1)$$

where x is the layer thickness, t the reaction time and k is proportional to the diffusion coefficient [6], and

$$k = k_0 \exp(-Q/RT) \quad (2)$$

where Q is the activation energy, R the gas constant and T the absolute temperature. Equation 1 is usually derived for a planar system. Its applicability to cylindrical geometries where the V_3Ga layer is small has been verified [4, 7]. In some of the cases where the equation fails to hold, there is a significant reduction of gallium concentration as the reaction proceeds. Equation 2 is the well-known Arrhenius equation.

Substituting Equation 1 into Equation 2, we get for the time to grow a 1 μ m thick V_3Ga layer

$$t_1 = 10^{-8} k_0^{-1} \exp(Q/RT). \quad (3)$$

Plots of $\log t$ versus $1/T$ (see Fig. 1) show that the data under study satisfy Equation 3 reasonably well. The value of the activation energy is, however, dependent on the concentration of gallium available for diffusion. Critchlow *et al.* have shown that t_1 is, in fact, an exponential

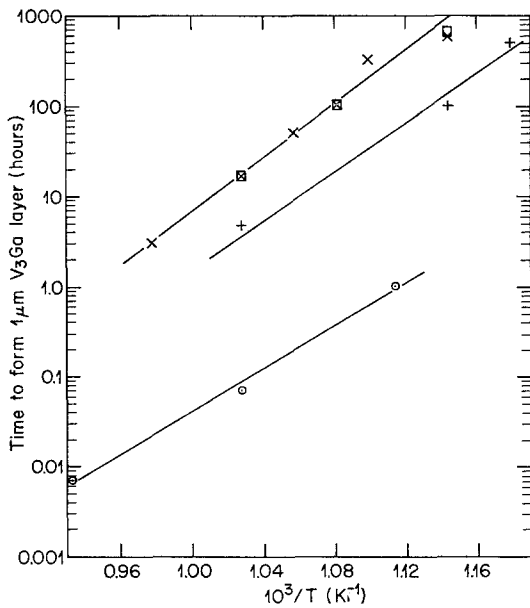


Figure 1 A plot of the time to grow a 1 μm V₃Ga layer versus (temperature)⁻¹. Data are taken from Critchlow *et al.* [5] (□), Suenaga and Sampson [1] (×), Howe *et al.* [4] (+), and Tachikawa *et al.* [2] (○).

function of the concentration *X*. We now examine the data quantitatively.

We expand the activation energy in a Taylor series, and retain only the linear term, i.e. we write

$$Q(X) = Q_0 + \alpha X \quad (4)$$

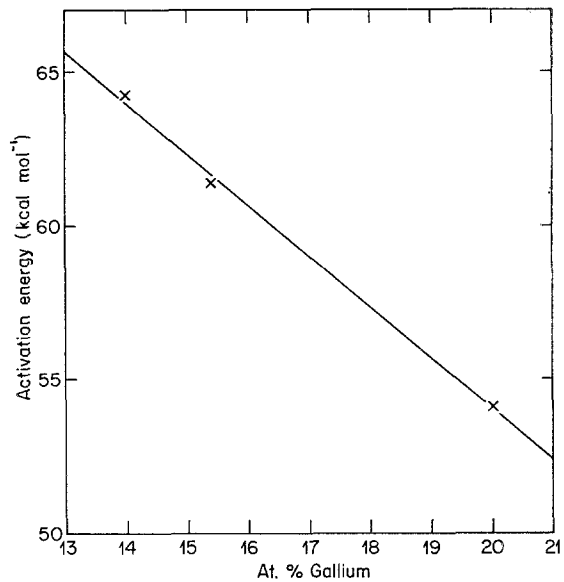


Figure 2 The activation energy for gallium diffusion in the system vanadium/gallium-copper as a function of gallium concentration.

(values of *X* as percentages are used in the calculations). Substituting Equation 4 into Equation 3, we get

$$t_1 = 10^{-8} k_0^{-1} \exp Q_0/RT \exp \alpha X/RT. \quad (5)$$

Thus at a fixed temperature, we have the required exponential dependence of *t*₁ on concentration.

The constant *Q*₀ has a special significance, it is the activation energy for the self-diffusion of

TABLE I A tabulation of the calculated and measured times required to grow a 1 μm layer of V₃Ga at different temperatures and for different concentrations of gallium in the matrix

At. % Ga	Temperature (K)	Time (h) measured	Time (h) calculated	% deviation
14%	973	18	14.4	-25%
	923	96	86.4	-11%
	873	~650	586	~-12%
14%	1023	3	2.85	-5%
	973	17	14.4	-18%
	948	40	34.4	-16%
	923	100	86.4	-16%
	908	240	154	-56%
	873	600	586	-2%
15.4%	973	4.8	4.3	-12%
	873	100	166	+40%
	848	500	473	-6%
20%	1073	0.007	0.006	-16%
	973	0.07	0.081	+16%
	898	1	0.84	-19%

vanadium. As mentioned previously, k_0 is related to the diffusion coefficient and may be expected to be the same for each sample.

In order to calculate k_0 , Q_0 and α from the available data, we begin with the plots of Fig. 1. Since there are more data points at 14 at. %, we use a least square fit on this curve to obtain k_0 . The average value of $Q(X)$ for each curve is then calculated. Fig. 2, a plot of $Q(X)$ versus X , shows a linear relation between $Q(X)$ and X . A least square fit to this curve gives Q_0 and α . The values of k_0 , Q_0 and α are found to be $45.6 \text{ cm}^2 \text{ sec}^{-1}$, $87.3 \text{ kcal mol}^{-1}$ and $-1.666 \text{ kcal mol}^{-1}$ respectively. The negative value for α is to be expected since, at low concentrations, diffusion occurs less rapidly.

Equation 5 now becomes

$$t_1 = 2.2 \times 10^{-10} \exp(87300 - 1666X)/RT. \quad (6)$$

As a check on the accuracy with which this formula reproduces the original data, we have tabulated the quoted times, times calculated from Equation 6 and the percentage deviation in Table I.

In most instances the agreement between experiment and calculation is within 10 to 20%. This is remarkable when one considers that (1) the range of times encountered covers five decades and (2) the sensitivity of Equation 6 to small changes in Q_0 , α and T . For example, a 1% decrease in α gives almost perfect fit for the 14 at. % data.

It is interesting to compare the directly measured values of Q_0 with the present value.

Most direct measurements of Q_0 are taken at higher temperatures, 900 to 1833°C , where Q_0 is not completely temperature independent but varies from 74 to 99 kcal mol^{-1} [8]. The present value, $87.3 \text{ kcal mol}^{-1}$, is thus reasonable.

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SEM characterization of fatigue crack tip deformation in stainless steel using a positive replica technique

Three measurable parameters have been correlated extensively in attempting to understand fatigue crack growth: (1) macroscopic growth rate (da/dN); (2) striation spacing; (3) plastic zone size. However, certain factors crucial to the linking of these quantities, including crack tip opening displacement (CTOD), crack tip configuration, and the mechanism of incremental crack growth, often have been lacking. This note describes a technique for obtaining this information through the replication of loaded fatigue crack tips, and crack tip yielding in 304 stainless steel is discussed.

Recently Wu *et al.* [1], reported the development of a technique for obtaining positive metal replicas of non-conducting materials such as polymers, for observation in the SEM. The writers have been using the same technique, but with the above problem in mind. Single-edge-notched specimens containing fatigue cracks are cycled under load control; at various stress intensity levels, cycling is suspended. Using Borden methyl acetate replicating material, negative replicas are obtained of the crack tip region in both the loaded and unloaded condition. (COD measurements obtained using a clip-on displacement gauge provide an estimate of the accuracy of the replicated features. A series of experiments during which COD was monitored both under cyclic loading, and also as a