quantities between the thermal analysis and resistivity data. These issues need to be resolved first.

In conclusion, a method for evaluating aging precipitation kinetics and potential using DSC curves without the need for peak separation or considering individual precipitation phases is possible, if accurate calorimetry data are available.

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Diffusion Coefficients for Modeling the Heat Treatment of Ti-6Al-4V

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Values of the diffusivity of aluminum and vanadium that can be used for engineering-oriented calculations of the diffusional growth of primary alpha during the heat treatment of Ti-6Al-4V were established using diffusion couples consisting of various Ti-Al-V alloys. After taking compositional influences into account using thermodynamic correction factors, the pertinent diffusivities in the ternary alloy were found to be approximately 80 pct of those previously estimated from tracer or impurity (binary) diffusion experiments.

A wide range of properties can be developed in alpha/beta titanium alloys such as Ti-6Al-4V *via* thermomechanical processing of conventional ingot-metallurgy products. The principal objective of primary mill processing is to develop a uniform, fine microstructure of equiaxed, primary alpha in a matrix of transformed beta. During subsequent part forging and final heat treatment in the two-phase (alpha/beta) field, the volume fraction and size of the primary alpha and the fineness of the colony-alpha matrix microstructure are determined by the choice of process variables. In particular, careful selection of the peak (soak) temperature and the cooling rate during final heat treatment provides the most direct method of controlling such microstructural features.

In a recent investigation,[1] it was shown that the growth of primary alpha during cooling in the alpha/beta field is controlled by diffusion of solutes through the beta matrix. Hence, a diffusion model was developed to predict the growth of the primary alpha and the decomposition of the beta matrix (to form secondary platelet alpha) during final heat treatment. The model made use of an exact solution of the one-dimensional diffusion equation[2,3] and was validated *via* a series of induction heat treatments on Ti-6Al-4V. The diffusion coefficients used in the calculations were based on impurity (aluminum) or tracer (vanadium) diffusion measurements for binary beta-titanium alloys.[4,5] For the nominally three-component Ti-6Al-4V alloy, the binary diffusion coefficients were adjusted using thermodynamic correction factors.[6,7]

The objective of the present work was to verify the accuracy of the diffusion coefficients that should be used in diffusion calculations for the alpha/beta heat treatment of Ti-6Al-4V specifically. For this purpose, a series of alloys of various beta-phase Ti-Al-V compositions were made *via* nonconsumable arc melting of cigar-shaped samples. The specific alloy chemistries (Table I) were selected based on previous measurements of the composition of the beta phase in Ti-6Al-4V at various temperatures (Figure 1). Each cigar was melted/remelted 6 times, then encapsulated in a quartz capsule and heat treated at 954 °C for 24 hours followed by oil quenching to ensure chemical homogeneity. The final beta grain size in each cigar was of the order of 4 mm.

Four different diffusion-couple combinations were fabricated to establish a so-called "effective" diffusivity of aluminum (A1/B1, A4/B4, and A5/B5) or vanadium (A2/B2) in a beta

Table I. Composition (in Weight Percent) of Diffusion-Couple Alloys

Sample	Al	V	O	Fe
A1	1.99	7.48	0.093	<0.01
B1	4.95	7.52	0.106	<0.01
A2	3.98	7.10	0.101	0.03
B2	4.08	9.93	0.114	<0.01
A4	2.01	7.59	0.19	0.10
B4	5.03	7.51	0.20	0.10
A5	1.06	12.67	0.12	<0.01
B5	3.96	12.73	0.08	<0.01

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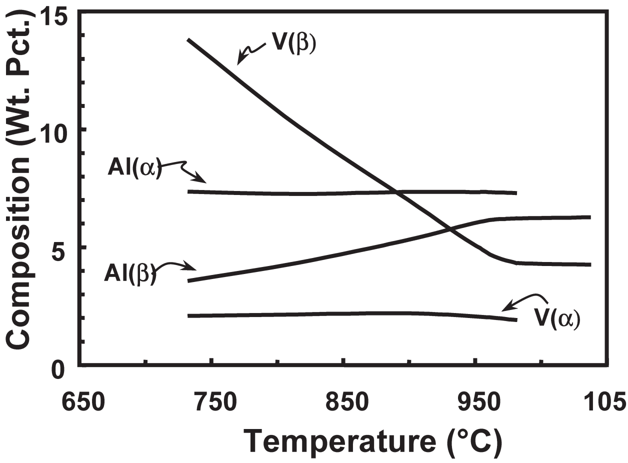


Fig. 1—Compositions of the alpha and beta phases in Ti-6.4Al-4.2V-0.14Fe-0.19O determined *via* wavelength-dispersive spectroscopy.[1]

titanium matrix containing titanium, aluminum, and vanadium as the principal alloying elements (Table I). Couples A1/B1 and A2/B2 were melted to a low-oxygen, low-iron specification. The effect of higher oxygen and iron on aluminum diffusion was established using the compositions A4/B4. In addition, the A5/B5 couple was used to determine the effect of high vanadium content on aluminum diffusion.

Each diffusion couple consisted of a pair of disks, which had been electric-discharge machined from the corresponding cigars and whose mating faces were metallographically polished. The disks were held in intimate contact by the pressure applied by a co-axial rod of tungsten, whose thermal expansion coefficient is less than that of titanium. The rod, whose ends were upset using TIG welding, passed through holes drilled through the disks and more massive backing bars of Ti-6Al-4V (Figure 2). One end of each of the two backing bars was radiused slightly on the face in contact with the diffusion couple in order to ensure perfect alignment of the couple components. After assembly, each diffusion couple was encapsulated in an evacuated quartz tube. Heat treatment comprised a preheat at 425 °C for 1 hour (to prevent thermal shock and failure of the tungsten rod whose ductile-brittle transition temperature ≈200 °C), quick transfer to a furnace operating at the desired diffusion temperature, and water quenching after holding for a preset time. The specific heat treatments comprised 120, 72, or 48 hours at temperatures of 843 °C, 899 °C, or 954 °C, respectively. Following heat treatment, the dimensions of the samples were measured to confirm that no deformation, which could have introduced dislocations and thus high-diffusivity paths, had been imposed. Subsequently, each sample was sectioned axially and metallographically prepared for composition measurements *via* wavelength-dispersive spectroscopy (WDS) in a JEOL* 733 Superprobe. The specific paths for the microprobe traverses were selected to stay well away from the widely spaced beta grain boundaries and thus to obtain concentration profiles that were indicative of bulk diffusion of the solutes.

The WDS data revealed a classical sigmoidal variation of aluminum (couples A1/B1, A4/B4, and A5/B5) or vanadium (couple A2/B2) composition with position. The corresponding variations of vanadium (couples A1/B1, A4/B4, and A5/B5) or aluminum (couple A2/B2) were negligible, thus indicating that their corresponding activities were essentially unaffected by the variation of the principal solute which had been diffusing. Hence, the aluminum (couples A1/B1, A4/B4, and A5/B5) or vanadium (couple A2/B2) concentration profiles were analyzed using the Boltzmann–Matano analysis[7] to identify first the Matano interface and then the diffusivity as a function of location/local concentration. Because the diffusivity values appeared to be a relatively weak function of concentration in a given diffusion couple, the measured concentration profiles were also compared to "calibration-curve" plots of the error function (erf) solution for the normalized concentration ($C = (c - c_{A_\infty})/(c_{B_\infty} - c_{A_\infty})$) as a function of distance (x) and time (t) in binary systems,[7,8] *viz.,*

$$C(x, t) = (1/2)\{1 + \operatorname{erf}(x/2\sqrt{Dt})\} \qquad [1]$$

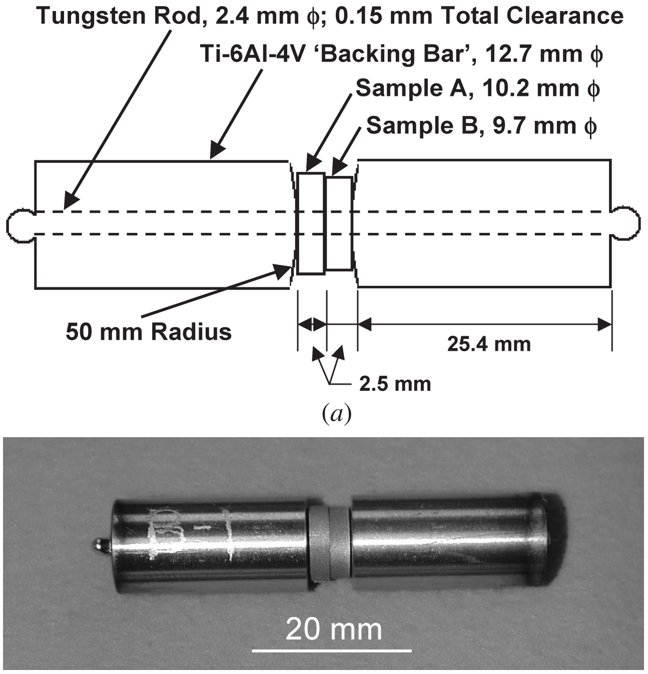
in which c_{A_∞} and c_{B_∞} denote the solute concentrations in alloys A and B, respectively, at infinite distance x from the diffusion couple (Matano) interface, and D is the diffusivity. From such comparisons (an example of which is shown in Figure 3), the best-fit values of diffusivity were obtained (Table II).

At a given temperature, the measured values of the diffusivity of aluminum and vanadium in ternary Ti-Al-V alloys (Table II) were found to be very similar. The specific values of the diffusivity of aluminum appeared not to be affected substantially by the oxygen or iron level, but were lowered when the vanadium content increased from 7.5 to 12.7 wt pct.

Activation energies Q_d for solute diffusion were estimated from the expression

$$Q_d/R = [\ln (D_2/D_1)][(1/T_1) - (1/T_2)] \qquad [2]$$

in which D_1 and D_2 connote the diffusivity at temperatures T_1 and T_2 (in Kelvin), respectively. The values of activation



(*a*)

(*b*)

Fig. 2—Diffusion-couple assembly used in the present work: (*a*) sample drawing and (*b*) photograph of finished assembly.

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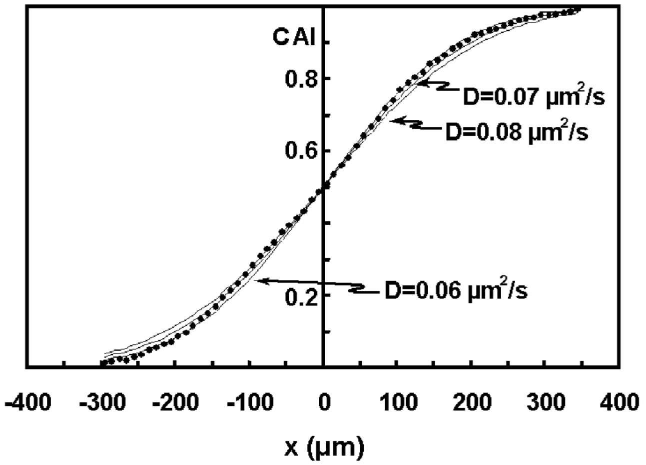


Fig. 3—Normalized aluminum concentration C_{Al} *vs* position for an A1/B1 diffusion couple annealed at 954 °C for 48 h.

Table II. Diffusion-Coefficient Measurements

Diffusion Couple	Alloying Element	D (954 °C) ($\mu m^2/s$)	D (899 °C) ($\mu m^2/s$)	D (843 °C) ($\mu m^2/s$)
A1/B1	aluminum	0.065	0.035	—
A4/B4	aluminum	0.060	~0.035	—
A5/B5	aluminum	0.045	0.025	0.0125
A2/B2	vanadium	0.050	0.025	—

energy (in kJ/mol) so obtained were 133 (A1/B1), 116 (A4/B4), and 131 (A5/B5) for aluminum diffusion and 149 (A2/B2) for vanadium diffusion. These values are comparable to previous measurements of 150 kJ/mol for aluminum[4] and 145 kJ/mol for vanadium.[5]

The pertinent values of diffusivity for use in modeling the heat treatment of Ti-6Al-4V were derived using thermodynamic correction factors, $1 + (\partial \ln \gamma_i/\partial \ln X_i)|x_j$, in which the γ_i and X_i denote the activity coefficient and mole fraction of component i, and the partial derivative is taken at fixed values of the mole fractions of the other components.[7,8] These correction factors were estimated using the PANDAT* code and the appropriate database for titanium alloys. The values of the correction factors for the diffusion-couple alloys (Table III) were slightly lower than those estimated for the equilibrium beta-phase composition for Ti-6Al-4V (Table IV).* Hence, each of the measured diffusivities was multiplied by a factor equal to the ratio of the correction factor of the pertinent solute in the beta phase in Ti-6Al-4V to that for the diffusion-couple alloy. The diffusivities adjusted in this manner are summarized in Figure 4.

The values of the diffusivities of aluminum and vanadium from the present work are very similar to those determined

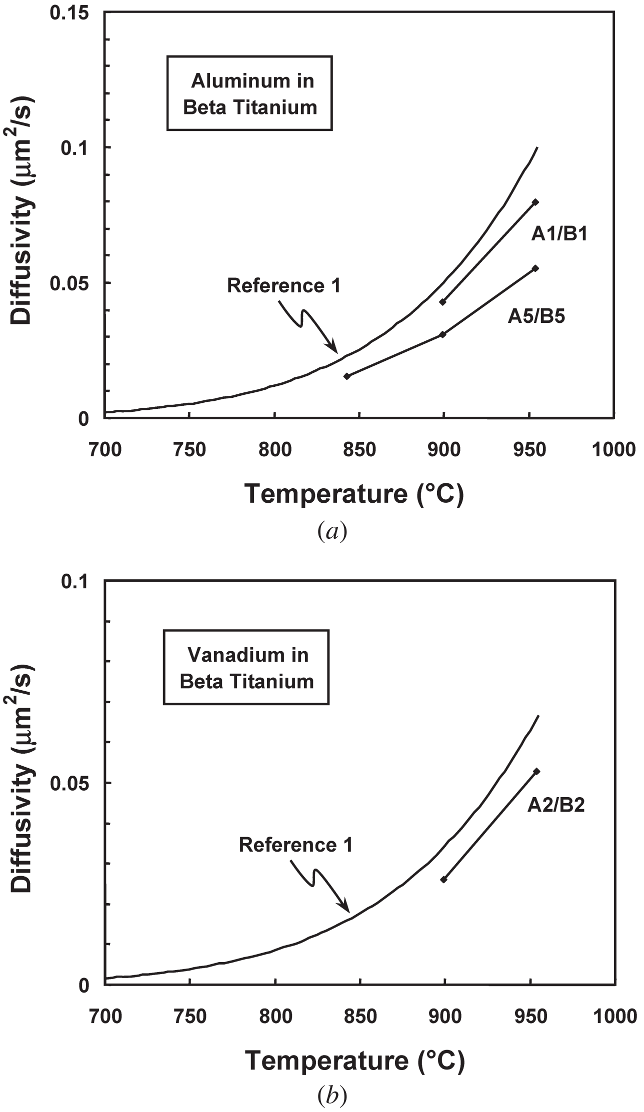
Table III. Thermodynamic Correction Factors

Diffusion Couple	Alloying Element	954 °C	899 °C	843 °C
A1/B1	aluminum	1.73	1.79	1.91
A4/B4	aluminum	1.73	1.79	1.91
A5/B5	aluminum	1.76	1.81	1.87
A2/B2	vanadium	0.86	0.85	0.84

Table IV. Equilibrium Composition and Thermodynamic Correction Factors (TCFs) for the Beta Phase in Ti-6Al-4V*

Temperature (°C)	Beta Composition (Wt Pct)	TCF: Aluminum	TCF: Vanadium
954	6.1Al-5V	2.12	0.91
899	5.3Al-7V	2.20	0.88
843	4.7Al-9V	2.26	0.84

*For an alloy with an overall composition of Ti-6.42Al-4.2V-0.19O.[1]



(*a*)

(*b*)

Fig. 4—Comparison of the diffusion coefficients measured in the present work to those used in Ref. 1: (*a*) aluminum and (*b*) vanadium.

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*PANDAT is a trademark of CompuTherm LLC, Madison, WI.

*Although the composition of the beta phase deviates from the equilibrium value during continuous cooling, such deviations for typical cooling rates lead to small changes in the thermodynamic correction factor, especially at higher temperatures, at which most of the diffusional growth occurs due the higher values of the diffusion coefficients.

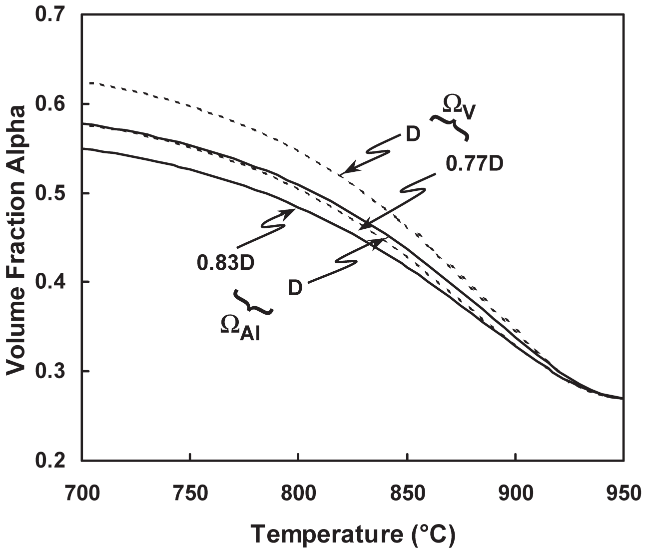

Fig. 5—Diffusion model predictions of the volume fraction of alpha in Ti-6Al-4V as a function of temperature, assuming a peak (soak) temperature of 955 °C, a cooling rate of 42 °C/min, and an initial particle radius of 4.5 μm. Diffusion calculations were performed assuming growth was controlled by either the aluminum supersaturation (Ω_{Al}) or the vanadium supersaturation (Ω_V).

by others using binary diffusion couples and those used for the diffusion modeling described in Reference 1 (Figure 4). Specifically, the diffusivity of aluminum in beta titanium (also containing vanadium at levels typical of that in Ti-6Al-4V) determined in the present work is approximately 0.83 times that of aluminum estimated previously from the corresponding binary alloy [$D_{Al}(\mu m^2/s) = 2.4 \times 10^5 \exp(-18{,}040/T(K))$]. Similarly, the diffusivity of vanadium in beta titanium (also containing aluminum at levels typical of that in Ti-6Al-4V) is approximately 0.77 times that of vanadium in the corresponding binary alloy [$D_V(\mu m^2/s) = 10^5 \exp(-17{,}460/T(K))$]. The effect of such differences in the diffusivity of aluminum or vanadium on predictions of the growth kinetics of primary alpha for a peak temperature of 955 °C and a cooling rate of 42 °C/min is shown in Figure 5. The effect is seen to be small in quantitative terms.

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High-Temperature Fatigue Crack Growth Behavior of 17-4 PH Stainless Steels

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The fatigue crack growth (FCG) behavior was investigated for 17-4 PH stainless steels in three heat-treated conditions, *i.e.*, unaged (condition A), peak-aged (condition H900), and overaged (condition H1150), at temperatures ranging from 300 °C to 500 °C. The high-temperature fatigue crack growth rates (FCGRs) of condition H1150 were increased with an increase in temperature. However, for conditions A and H900 tested at 500 °C, the FCGRs were lower than the lower temperature ones. At 300 °C and 400 °C, H1150 and H900 generally showed the lowest and highest FCGRs, respectively, with condition A demonstrating behavior between the two. At 500 °C, the FCGR curves for all material conditions merged together. The anomalous FCG behavior of 17-4 PH stainless steels at 500 °C was mainly caused by an *in-situ* precipitate-coarsening effect during test.

Precipitation-hardening stainless steels have been widely used as structural components for various applications, such as nuclear, chemical, aircraft, and naval industries, due to their excellent mechanical properties, good fabrication characteristics, and excellent corrosion resistance. Of the former, 17-4 PH stainless steel is currently one of the most commonly used alloys.[1] 17-4 PH is a typical martensitic precipitation-hardening stainless steel and most often supplied from the mill in solution-annealed condition (condition A). By applying suitable heat treatments in the temperature range of 482 °C to 621 °C, a wide range of mechanical properties can be obtained.[1–6] In general, the maximum strength and hardness values are obtained after aging at 450 °C to 510 °C, during which the precipitation of coherent copper-rich clusters occurs.[1,2,3] Aging at higher temperatures (above 540 °C) results in the precipitation of

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