T_{MEAN} °C	ΔT °C	P_{MEAN} (cm)	Steady State log P_h/P_c	$\Delta \bar{H}$ cal/g atom	Q^* cal/g atom
405	10	55	+0.0032 ± 0.0005	−1700 ± 250	+1400 ± 300
492	15	55	+0.0005 ± 0.0005	−1500 ± 200	+1450 ± 300
546	22	55	−0.0026 ± 0.0005	−1400 ± 200	+1600 ± 300

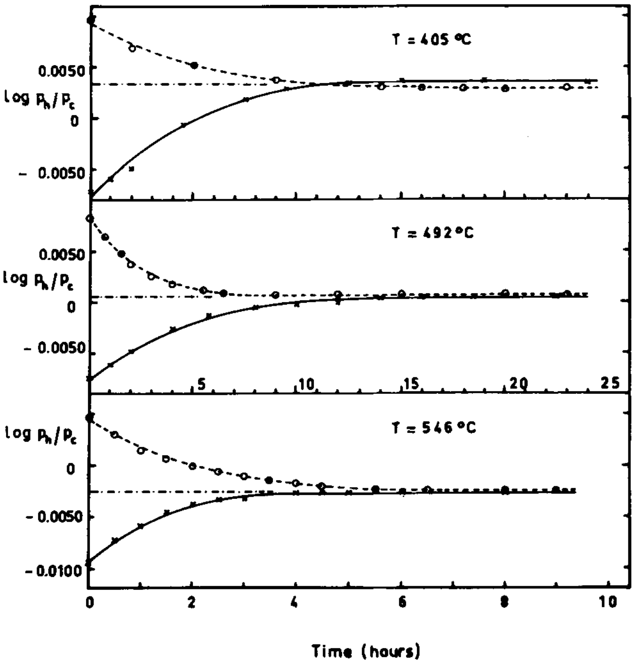

Fig. 2—ln P_h/P_c as a function of time for the temperatures investigated.

investigations is shown schematically in Fig. 1. Basically it consisted of a specimen assembly, which contained the palladium membrane (1.4 cm diam, 0.1 cm thick), a heating and a cooling block to provide the temperature gradient, and a hot and cold side gas volume. The palladium used was 99.99 pct Pd and hydrogen was employed directly from the cylinder. The procedure followed when making a run consisted of adjusting the hydrogen pressures on both sides of the membrane to values close to the steady-state pressure distribution and then following the variation of the quantity ln P_h/P_c with time to the final stationary state. For each particular mean membrane temperature, the steady state was approached from both directions. That is, from initial ln P_h/P_c values greater than and smaller than the steady-state value. In this way an average ln P_h/P_c was determined.

Fig. 2 shows representative results for temperatures investigated. Experimental details are listed in the table of this figure together with the calculated heats of transport. The solubility data of Sieverts[4] and Sieverts and Zapf[5] were used to evaluate the heat of solution at each temperature. It is evident from the tabulated values of Q^* that over the temperature range studied, thermomigration of hydrogen in palladium is small and effectively independent of temperature. An average Q^* of +1.5 ± 0.5 kcal per g atom can be assigned to the system for the entire range.

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Experiments on Macrosegregation and Freckle Formation

R. MEHRABIAN, M. A. KEANE, AND

M. C. FLEMINGS

In a series of recent papers, we have concluded that a number of industrially important types of macrosegregation are caused by the same basic mechanism, interdendritic fluid flow. The flow is caused by solidification contractions, gravity acting on a fluid of variable density, or both. Types of segregation caused by this mechanism include centerline segregation, inverse segregation, banding and channel-type segregates, such as "freckles".[1–5]

This note presents direct experimental evidence that gravity induced interdendritic fluid flow leads to macrosegregation. In two experiments on horizontal unidirectional solidification, segregation is found to agree closely with that predicted by theory. In a third experiment, channel-type segregates are found under conditions qualitatively predicted by theory.

The basic apparatus and procedure have previously been described.[3] The ingots cast were horizontally, unidirectionally solidified, Fig. 1(*d*). Heat was extracted through a water-cooled chill at one extremity while the sides and top were insulated with molding material heated to above the melting point of the alloys cast. The ingots were of uniform cross-section, 5 by 25 by 10 cm high with a 5 by 5 by 10 cm high riser on the end. In one ingot, Al-9.5 pct Cu, six thermocouples were placed along the horizontal ingot centerline to obtain a continuous record of solidification. Movement of liquidus and solidus isotherms obtained from these thermal data are shown in Fig. 2(*c*). For calculations described below, isotherm movement was assumed to be the same in the Al-4.4 pct Cu ingot.

Alloys were prepared from high purity aluminum (99.99 pct Al), Al-Cu master alloy (50 pct OFHC Cu, 50 pct high purity Al). Degassing was accomplished with chlorine, which was bubbled through the melt for 15 min at 100° to 150° F above the liquidus temperature. Melt composition was determined by chemical analysis of two specimens taken before and after pouring. Macrosegregation in the ingots cast was determined by both wet chemical and X-ray fluorescence analysis. Details of the X-ray fluorescence method have previously been described.[3]

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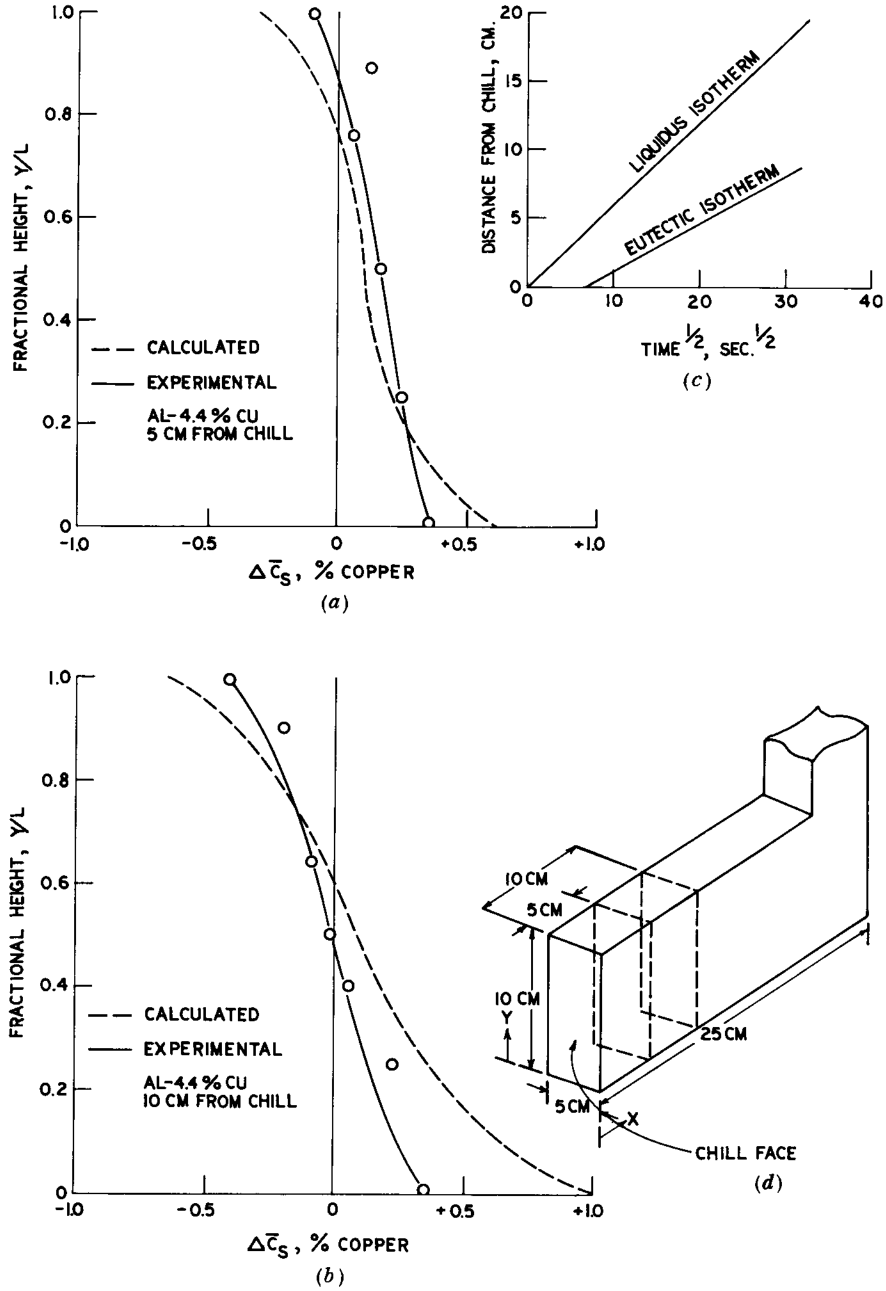

Fig. 1—Macrosegregation in horizontal unidirectionally solidified Al-4.4 pct Cu ingot. (*a*) and (*b*) show experimental data for two locations, (*c*) shows movement of isotherms, and (*d*) is a sketch of the ingot.

Experimental results for two ingots, Al-4.4 pct Cu and Al-9.5 pct Cu, are summarized in Figs. 1 and 2, respectively. Figs. 1(*a*) and 1(*b*) show copper compositions for the Al-4.4 pct Cu ingot. Composition variation, $\Delta \bar{C}_S$ (*i.e.*, macrosegregation) are plotted vs distance along the ingot height. Fig. 1(*a*) is for the locations 5 cm from the chill and Fig. 1(*b*) for locations 10 cm from the chill. Also in Fig. 1(*a*) and 1(*b*), dashed curves shown are segregations calculated by numerical analysis as described below.

Fig. 2 shows experimental and calculated segregation in the Al-9.5 pct Cu ingot, for two locations 5 and 8 cm from the chill. The segregation is of the same form as that in the Al-4.4 pct Cu ingot, but of greater magnitude. Again, there is approximate agreement of the experimental results with those calculated as described below.

A third unidirectional ingot, Al-20 pct Cu, was cast using a similar procedure except that rate of heat extraction was greatly reduced by heavily coating the chill with fiberfrax. Thus, isotherm velocities were lowered, cooling rate was decreased, and dendrite arm spacing increased. All of these factors favor enhanced segregation, leading ultimately to the formation of channel-type segregates ("freckles"). Fig. 3 shows a cross-section of this laboratory test ingot. The segregates which are readily seen are a direct laboratory simulation of the commercially well-known "freckles".[5] The relatively high copper content of this ingot makes the "freckles" clearly visible (because of the large amount of eutectic in the alloy). Similar "freckles" have been obtained under similar thermal conditions at lower copper content.

In the previous work,[5] hydrodynamics of interdendritic fluid flow were considered quantitatively. In that work it was concluded that flow in the direction opposite to movement of isotherms lowered local composition, flow in the same direction as isotherms raised

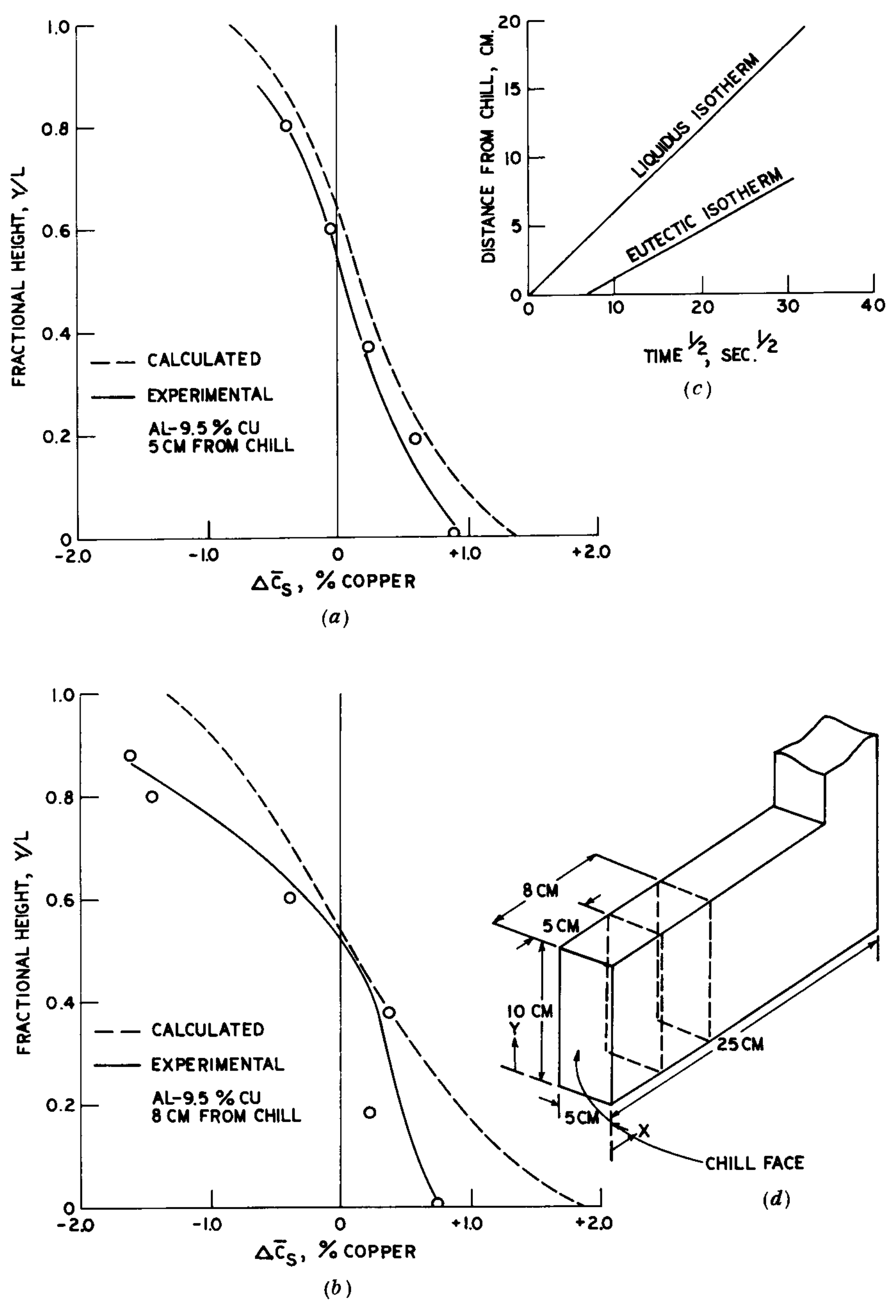

Fig. 2—Macrosegregation in horizontal unidirectionally solidified Al-9.5 pct Cu ingot. (*a*) and (*b*) show experimental data for two locations, (*c*) shows movement of isotherms, and (*d*) is a sketch of the ingot.

composition, and flow both in the same direction as isotherms and moving faster than isotherms resulted in "channeling" and formation of segregates such as "freckles". Numerical calculations of flow behavior and resulting segregation were made for some simple steady-state cases of two-dimensional fluid flow.

In this work, in order to compare our experiments with theory, it was necessary to extend the foregoing analysis to solution of the case of unsteady state heat flow. Consider the ingot of Fig. 1(*d*) solidifying unidirectionally with heat flow in the x direction and gravity acting in the y direction. In the previous steady-state treatment, the size of the liquid-solid "mushy" region was assumed constant. In calculations performed for this work, the width of the liquid-solid region was allowed to vary during solidification as experimentally observed, Fig. 1(*c*). The only essential change to accomplish this is that in Eqs. [7] and [17] of the previous paper,[5] ϵ and G are taken as a function of position and time. (ϵ is rate of temperature change and G thermal gradient.) Segregation is then estimated by assuming a value of γ for Eq. [13] of the previous paper:[5]

$$\gamma = \frac{1}{24 n\pi c^3} \qquad [1]$$

where n is the number of flow channels per unit area perpendicular to direction of flow and c is a geometric factor to account for the fact that channels are neither straight nor symmetrical. All other data necessary for solution of the differential equations by numerical methods were given in the previous paper.[5]

The value of γ used for all calculations (for both ingots) was 6×10^{-7} sq cm. This value was chosen to agree best with experiment. The value can be seen to be reasonable, however, since it corresponds to a value of c of 1.3 and n of 10^4 channels per sq cm. The value of c is about that often found for flow in porous media, and the value of n is of the order that would be expected if there were one channel between each pair of dendrite arms (dendrite arm spacings measured were in the range of 80 to 100 μ in the region 5 to 10 cm from the chill). Results of calculations are seen in Figs. 1 and 2 to agree approximately at both locations in the two ingots studied, even with the approximation of constant value of γ at all locations.

1) Direct experimental evidence is given that gravity-induced interdendritic fluid flow leads to macrosegregation in ingot solidification. Results of experiments are in agreement with theory.

2) It is shown that channel-type segregates (*e.g.*, "freckles") can be readily reproduced in small ingots in the laboratory, under conditions qualitatively predicted by theory.

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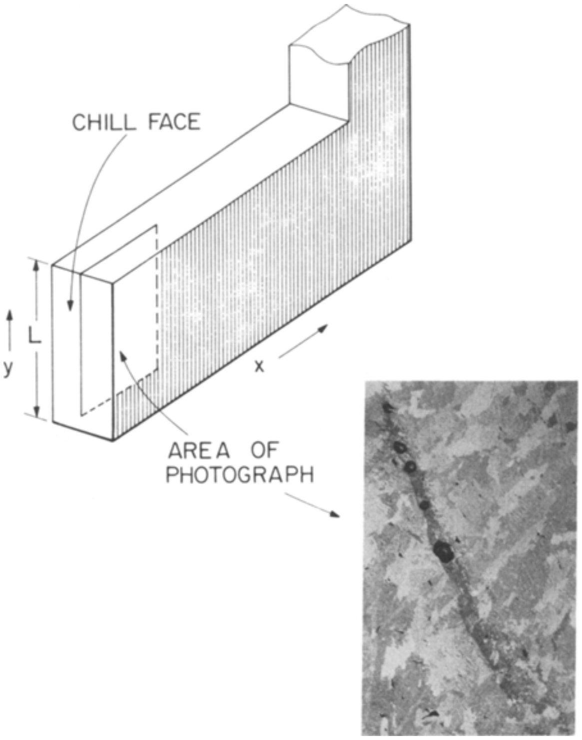

Fig. 3—Channel-type segregate ("freckle") in horizontal unidirectionally solidified Al-20 pct Cu ingot.

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Hydrogen Induced Sustained Load Crack Growth in Ti-6Al-4V

G. F. PITTINATO AND S. F. FREDERICK

THE mechanical properties of Ti-6Al-4V at near ambient temperature can be lowered by a hydrogen environment when the material contains a high stress concentration.[1-3] Fatigue crack propagation tests conducted in helium and hydrogen gas have shown that hydrogen increases the crack growth rate in Ti-6Al-4V in the temperature range of ambient to $-100°F$.[2,3] In the following study, it was found that a hydrogen environment can also induce sustained load crack growth in annealed Ti-6Al-4V at ambient temperature.

Flat tensile specimens containing a 1 in wide reduced section were machined from 0.080 in thick sheets of annealed ELI Ti-6Al-4V. A semielliptical, partial thickness crack measuring 0.100 in long was formed in the center of the reduced section in each specimen by using an eloxed starter notch and flexure fatigue cycling.[4] The sustained load specimens were tested in a sealed retort at ambient temperature in air and 25 psig pressure of hydrogen using gross stress levels of 82 and 110 ksi. Prior to applying the sustained load, the precracks in selected specimens were extended in hydrogen gas by using tension-tension fatigue. The degree of crack extension was determined by measuring the crack length through a viewing port in the test chamber. Following the sustained load tests, the specimens were stressed to failure in air and the fracture surfaces examined using both optical and electron microscopy.

The sustained load test results are summarized in Table I. Specimens A-28 and A-22 were tested in air to confirm that crack growth would not occur as a direct result of the high stress levels used in the sustained load tests. Examination of the specimens after

Table I. Tabulation of Sustained Load Test Results

Sample Number	Length of Precrack, in.	Sustained Load Test			Evidence Found of Sustained Load Crack Growth
		Stress, ksi	Time	Atmosphere	
A-28	0.100	110	96 hr	Air	No
A-22	0.124	110	220 hr	Air	No
	Extended to 0.141	110	113 hr	Hydrogen	No
A-37	0.100	110	96 hr	Hydrogen	No
A-35	0.100	82	112 hr	Hydrogen	No
A-41	0.112*	82	8 hr	Hydrogen	Yes
A-34	0.127*	82	116 hr	Hydrogen	Yes
A-88	0.126*	110	4 min	Hydrogen	Failed
A-62	0.115*	110	90 hr	Hydrogen	Yes
	Extended to 0.140*	110	11 min	Hydrogen	Failed

*Crack entended in hydrogen gas from 0.100 in. to length shown by using tension-tension fatigue.

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