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SUMMARY

A semiempirical relationship is presented which describes the extent of interaction between constituents in single-phase binary alloy systems having planar, cylindrical, or spherical interfaces. This relationship makes possible a quick estimate of the extent of interaction without lengthy numerical calculations. It includes two parameters which are functions of mean concentration and interface geometry. Experimental data for the copper-nickel system are included to demonstrate the usefulness of this relationship.

INTRODUCTION

In the analysis of diffusion controlled processes (e.g., the diffusion of planar protective coatings into substrate materials, the filament-matrix interaction in metal matrix composites, or the homogenization of powder compacts), the ability to predict the degree of interaction between different components, given some exposure conditions, is needed. In the past, the approach has been to solve the diffusion equation with the appropriate initial and boundary conditions (refs. 1 and 2). The solution to the diffusion equation is usually obtained by numerical methods such as finite-difference or infinite-series solutions except in limited cases where analytical solutions exist. However, the numerical methods involve extensive calculations, and a separate set of calculations is required for each composition and interfacial geometry of the material system being considered.

The purpose of this paper is to provide a single semiempirical relationship which describes the extent of interaction between the constituents in single-phase binary alloy systems having planar, cylindrical, or spherical interfaces. This relationship makes possible a quick estimate of the extent of interaction without lengthy numerical calculations. It includes two parameters which are functions of mean concentration and interface geometry. Experimental data for the copper-nickel system are included to demonstrate the usefulness of this relationship.

ANALYSIS

Figure 1 shows the nomenclature and schematic of the geometric models for planar, cylindrical, and spherical interfaces. The average concentration H of element B in the original B-rich region is a measure of the degree of homogenization at any time t. For the planar, cylindrical, and spherical geometries (denoted by the subscripts p, c, and s, respectively), H is given by

$$H_p = \frac{1}{R_B} \int_0^{R_B} C_B \, dr \qquad (1)$$

$$H_C = \frac{1}{R_B^2} \int_0^{R_B} C_B 2r \, dr \qquad (2)$$

$$H_S = \frac{1}{R_B^3} \int_0^{R_B} C_B 3r^2 \, dr \qquad (3)$$

where C_B is the volume fraction of element B at distance r, R_B is the thickness or radius of the B-rich region, and R_T is the total thickness or radius of the sample. (See fig. 1.) The degree of homogenization can also be expressed as the ratio of the amount of material transferred across the boundary at time t to the amount of material at $t = \infty$ (ref. 2). The relationship between this ratio F and H is given by

$$H = 1 - F(1 - \bar{C}_B) \qquad (4)$$

where $\bar{C}_B$ is the average volume fraction of element B in the specimen. The value of F varies from zero to unity whereas H varies from unity to $\bar{C}_B$.

If the diffusion coefficient D is assumed to be independent of concentration, the equation governing homogenization in single-phase binary alloy systems is given by

$$\frac{\partial C_B}{\partial t} = \frac{D}{r^m} \frac{\partial}{\partial r} \left(r^m \frac{\partial C_B}{\partial r} \right) \qquad (5)$$

where m is 0, 1, and 2 for planar, cylindrical, and spherical geometries, respectively. The initial and boundary conditions to be satisfied are

$$\left. \begin{array}{ll} C_B = 1 & (0 \leqq r \leqq R_B; \quad t = 0) \\[2mm] C_B = 0 & (R_B \leqq r \leqq R_T; \quad t = 0) \\[2mm] \dfrac{\partial C_B}{\partial r} = 0 & (r = 0 \quad \text{and} \quad r = R_T; \quad t > 0) \end{array} \right\} \qquad (6)$$

Solutions to equations (5) and (6) were determined for each geometry for different values of $\bar{C}_B$ by using a finite-difference technique (ref. 3). Values of H were plotted as a function of τ for each geometry and $\bar{C}_B$, where τ is a dimensionless parameter and is equal to the normalized diffusion time Dt/R_B^2. Several different equations were fitted empirically to the

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plotted values to determine the simplest expression that best described all data.

For the special case of planar geometry with $\bar{C}_B \to 0$, a simple closed-form solution exists for equations (5) and (6). In this case, the concentration of component B (ref. 4) is given by

$$C_B = \frac{1}{2}\left[\text{erf}\left(\frac{R_B - r}{2\sqrt{Dt}}\right) + \text{erf}\left(\frac{R_B + r}{2\sqrt{Dt}}\right)\right] \tag{7}$$

or

$$C_B = \frac{1}{2}\left[2 - \text{erfc}\left(\frac{R_B - r}{2\sqrt{Dt}}\right) - \text{erfc}\left(\frac{R_B + r}{2\sqrt{Dt}}\right)\right] \tag{8}$$

where erf and erfc are the error function and the error function compliment, respectively. The equation in terms of erfc is in a convenient form for the subsequent integration required in developing an expression for H_p, which is the homogenization parameter given by equation (1). By making use of the relation

$$\int_r^\infty \text{erfc}(\eta)\,d\eta = \frac{1}{\pi}e^{-r^2} - r\,\text{erfc}(r)$$

equation (1) reduces to

$$H_p = 1 - \sqrt{\frac{\tau}{\pi}}\left[1 + \sqrt{\frac{\pi}{\tau}}\,\text{erfc}\left(\sqrt{\frac{1}{\tau}}\right) - e^{-1/\tau}\right] \tag{9}$$

For this case, the empirical results were compared with those from the analytical solutions (eq. (9)) as well as with those from the finite-difference solutions.

RESULTS AND DISCUSSION

The following empirical equation gave results which were in good agreement with those obtained from the finite-difference analysis:

$$H = \bar{C}_B + (1 - \bar{C}_B)\exp(-p\tau^q) \tag{10}$$

Parameters p and q were evaluated for each geometry and value of $\bar{C}_B$ that were considered.

Typical results for planar geometry with $\bar{C}_B = 0.25$ are shown in figures 2 and 3, where the curves of H as a function of τ which were determined from equation (10) are compared with those from the finite-difference analysis. Curves are shown for different values of q (fig. 2) and p (fig. 3) to determine the sensitivity of H to these parameters. As can be seen, p = 1.15 and q = 0.65 gave results nearly identical to those from the finite-difference analysis. Similar calculations were carried out for cylindrical and spherical geometries, and in all cases equation (10) satisfactorily described the finite-difference results.

Table I shows the p and q values for all geometries considered. The quantity ΔH is the absolute difference between a finite-difference value and the corresponding value computed with equation (10). As can be seen from table I, the values for ΔH_{max} and ΔH_{av} (where the subscripts max and av denote maximum and average, respectively) are less than or equal to 0.033 and 0.012, respectively, with the exception of planar geometry with $\bar{C}_B = 0.01$, for which the values are as high as 0.070 and 0.025, respectively. The analytical solution (eq. (9)) could be used if greater accuracy were desired.

Figure 4 shows a plot of p and q as a function of $\bar{C}_B$ for each of the three geometries. Parameter p increases with increasing $\bar{C}_B$. Also, for a given concentration, the values of p for cylindrical and spherical geometries are, respectively, about 2 and 3 times as great as that for the planar geometry. However, parameter q has a maximum for each geometry. The values of $\bar{C}_B$ at the maxima are approximately 0.5, 0.3, and 0.22 for planar, cylindrical, and spherical geometries, respectively. For planar geometry, the curve of q as a function of $\bar{C}_B$ is symmetrical about $\bar{C}_B = 0.5$. This value of $\bar{C}_B$ corresponds to diffusion conditions where the thicknesses of the A and B regions are equal $(R_T = 2R_B)$. The asymmetry in the cylindrical and spherical curves is due to the complexities of the interface geometry.

Carpenter, Tenney, and Houska (ref. 5) have electroplated 8 μm of nickel onto one face of a (111) oriented copper single-crystal disk, annealed the specimen at 1173 K for 3/4, 2, and 5 hr, measured diffracted X-ray intensity after each anneal, and determined concentration profiles from the X-ray data by an absorption technique. Because the plating thickness $(R_B = 8 \text{ μm})$ is negligible when compared with the total thickness R_T, the degree of homogenization in this specimen can be calculated by using the values of p and q that correspond to $\bar{C}_B = 0$ (i.e., p = 0.55 and q = 0.50). The solid line in figure 5 denotes the variation of H with τ which was generated by using these p and q values in equation (10). For this planar geometry, the empirical curve is in reasonable agreement with the finite-difference and exact solutions as well as with the experimental data points. The diffusion coefficient D was taken as $0.2 \times 10^{-14} \text{ m}^2/\text{s}$, which corresponds to the nickel-rich concentration range (ref. 6). A slightly lower value of D would be more appropriate because $0.2 \times 10^{-14} \text{ m}^2/\text{s}$ corresponds to polycrystalline nickel whereas the present specimen consisted of nickel epitaxially deposited on

single-crystal copper. Renormalizing τ with the lower D value would move the experimental points toward lower τ values, making the agreement better.

Heckel (ref. 2) prepared compacted mixtures of elemental copper and nickel powders with different average compositions, annealed them in the 1223 to 1323 K temperature range for various lengths of time, and analyzed them for the degree of homogenization F. His homogenization results F for a sample with $\bar{C}_B = 0.11$ were converted to H by using equation (4). The results are shown in figure 6 and can be compared with the finite-difference and equation (10) results if a spherical geometry is assumed. The values of p (3.8) and q (0.66) used in equation (10) were obtained from figure 4 for $\bar{C}_B = 0.11$. As can be seen, the present empirical solution is in excellent agreement with the finite-difference solution and is in reasonable agreement with the experimental homogenization data on powder compacts.

Figure 7 shows the predicted homogenization values for specimens with cylindrical geometry and $\bar{C}_B = 0.01$, 0.50, and 0.75. No experimental data for long diffusion time could be found in the literature for the cylindrical geometry case although it would be of importance in the analysis of interaction in fiber-reinforced composites. (Herring and Tenney (ref. 7) have investigated diffusion between Ni filaments and a Cu matrix. However, the extent of interaction in their studies is not large enough to provide a meaningful check of the results shown in fig. 6.) The finite-difference solutions for $\bar{C}_B = 0.50$ and 0.75 are identical to the present empirical solution and are not shown for $\tau < 10^{-1}$ to avoid confusion. As can be seen, the present empirical solution is in good agreement with the finite-difference solution for all the values of $\bar{C}_B$ considered.

CONCLUSIONS

A semiempirical relationship has been developed which describes the extent of interaction between constituents in single-phase binary alloy systems with planar, cylindrical, or spherical interfaces. The relationship contains two parameters which are functions of mean concentration and interface geometry of the couple. The empirical solution is simple, easy to use, does not involve sequential calculations, and hence makes possible a quick estimate of the extent of interaction without lengthy calculations. Results obtained with the empirical relationship are in good agreement with results from a finite-difference analysis and with experimental results.

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TABLE I.- RESULTS OF CURVE FITTING FOR DIFFERENT $\bar{c}_B$

AND INTERFACIAL GEOMETRY

Geometry	$\bar{c}_B$	p	q	ΔH_{max}	ΔH_{av}
Planar	0.01	0.61	0.50	0.070	0.025
Planar	.10	.80	.55	.028	.012
Planar	.25	1.15	.65	.011	.004
Planar	.50	2.25	.69	.014	.007
Planar	.75	4.50	.63	.005	.001
Planar	.90	8.98	.56	.004	.002
Planar	.99	30.30	.43	.001	.000
Cylindrical	.01	1.62	.61	.033	.009
Cylindrical	.10	2.14	.65	.012	.004
Cylindrical	.25	3.05	.67	.020	.009
Cylindrical	.50	5.08	.66	.011	.005
Cylindrical	.75	8.42	.58	.005	.001
Cylindrical	.90	14.40	.52	.005	.002
Spherical	.01	2.95	.64	.013	.003
Spherical	.10	3.74	.66	.017	.008
Spherical	.25	5.13	.67	.020	.009
Spherical	.50	8.14	.65	.009	.003
Spherical	.75	13.19	.59	.007	.003
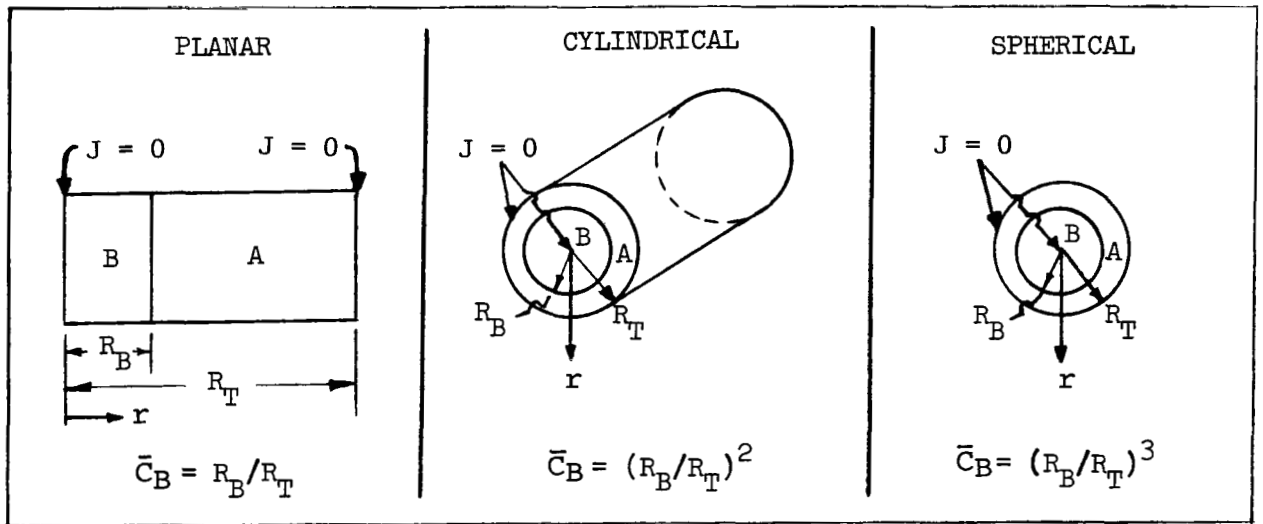
Figure 1.- Geometric models showing zero flux boundary conditions $(J = 0)$ and average concentration $\bar{C}_B$.
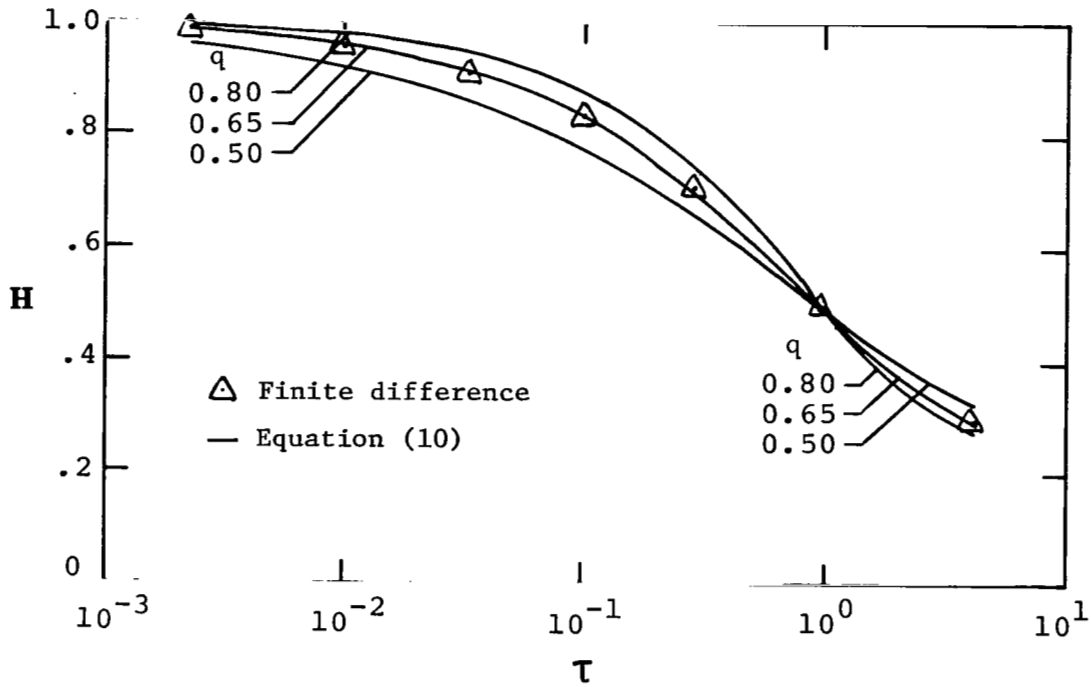
Figure 2.- Sensitivity of H to changes in parameter q for planar geometry with $\bar{C}_B = 0.25$ and $p = 1.15$.
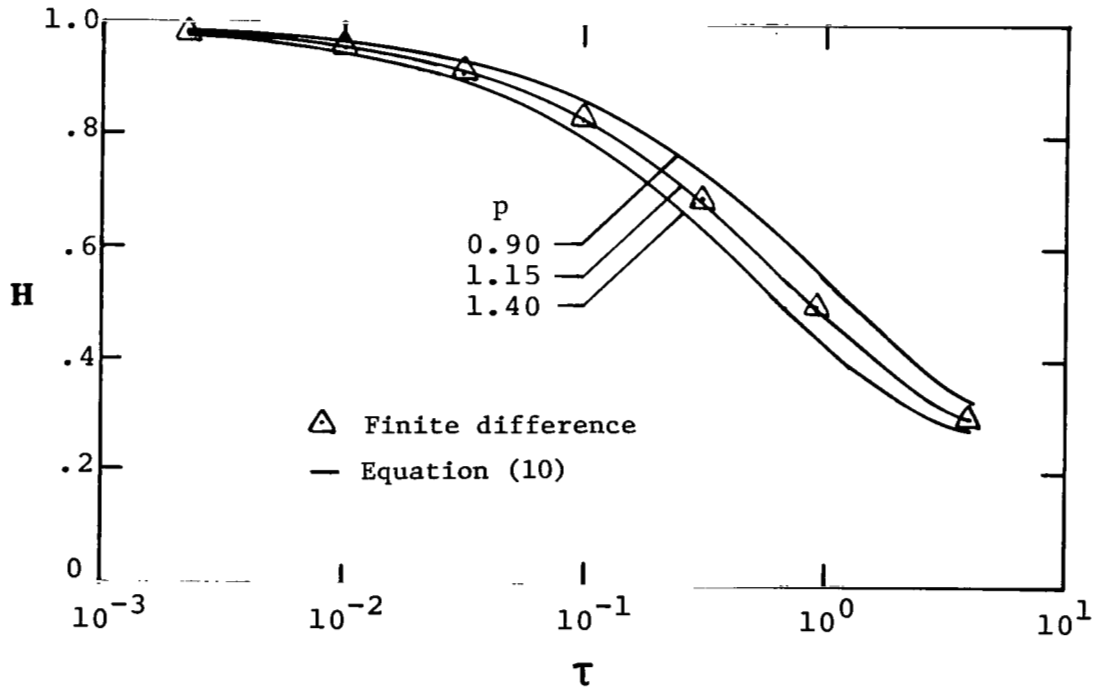

Figure 3.- Sensitivity of H to changes in parameter p for planar geometry with $\bar{C}_B = 0.25$ and $q = 0.65$.
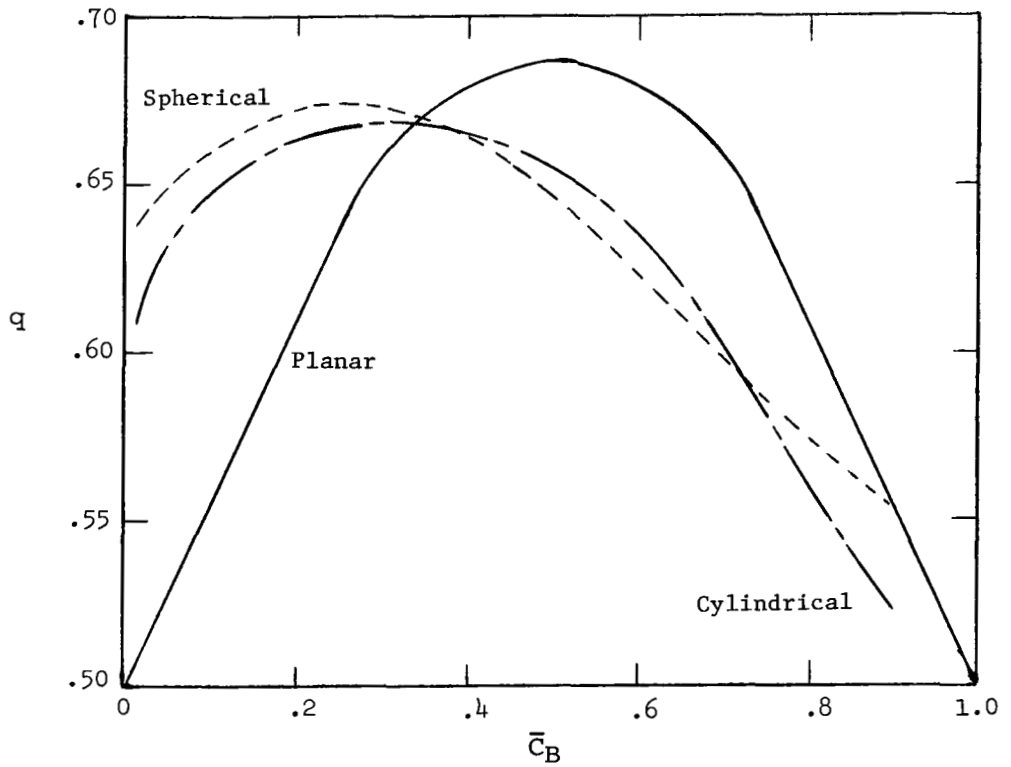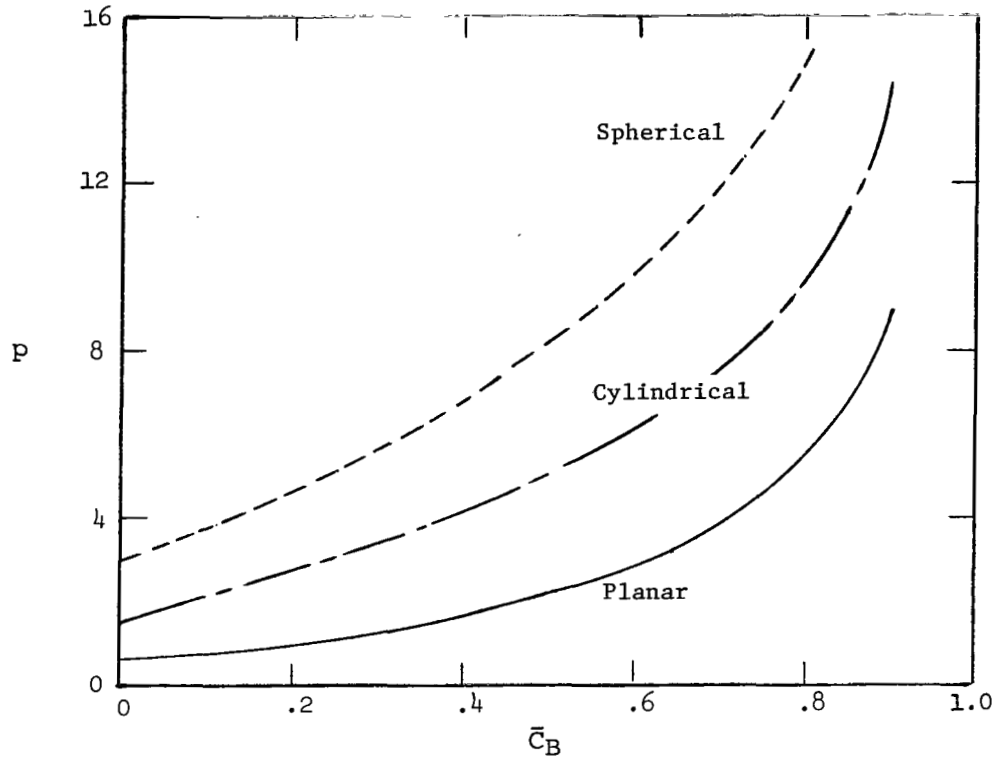
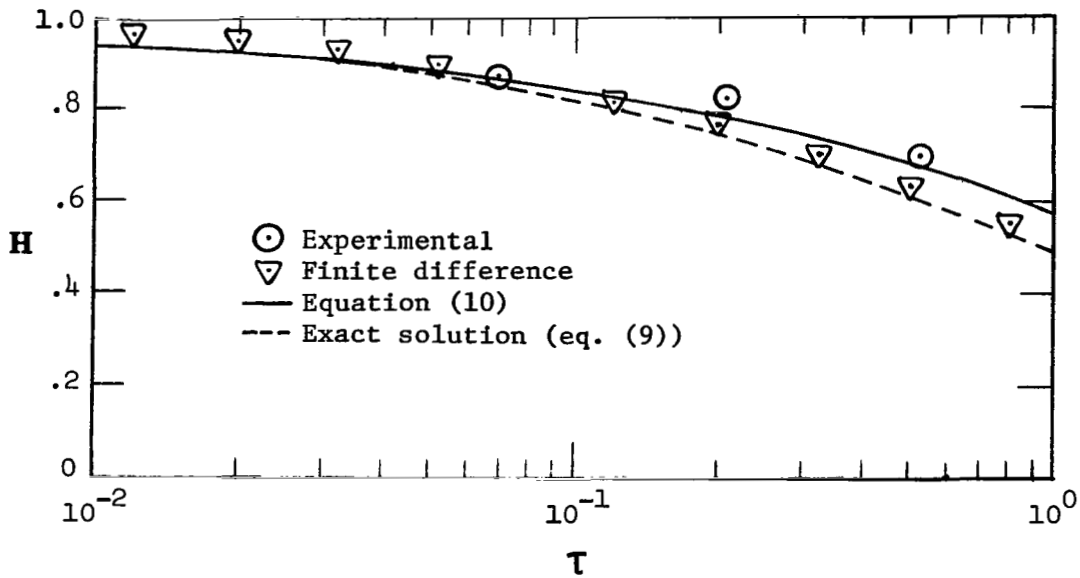Figure 4.- The p and q values to be used in equation (10).

Figure 5.- Experimental and predicted homogenization values for copper-nickel planar couple ($\bar{C}_{Ni} \simeq 0$).
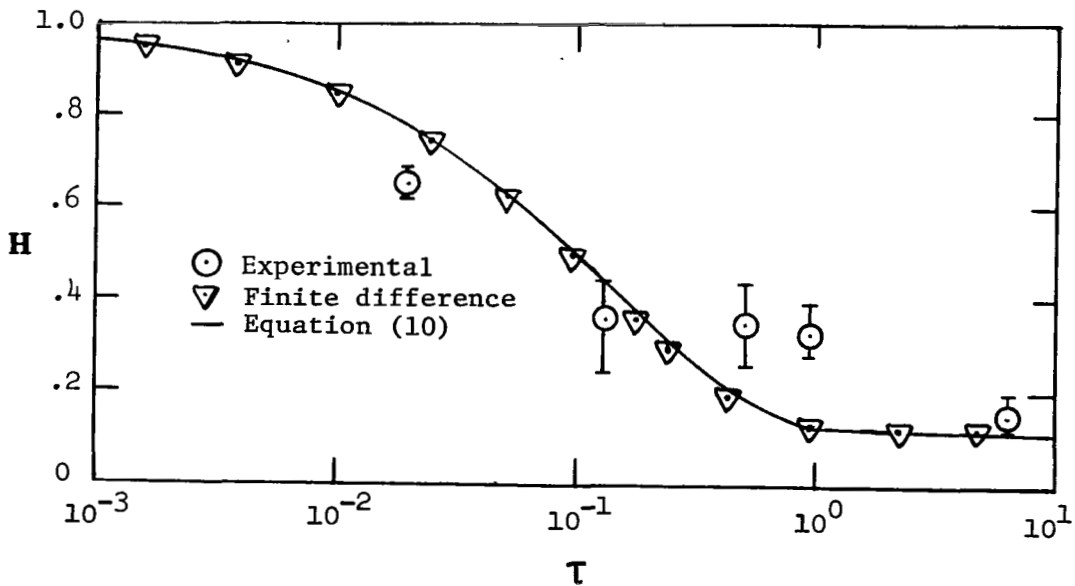

Figure 6.- Experimental homogenization data for copper-nickel powder compact and the predicted values if a spherical geometry is assumed ($\bar{C}_{Ni} = 0.11$).
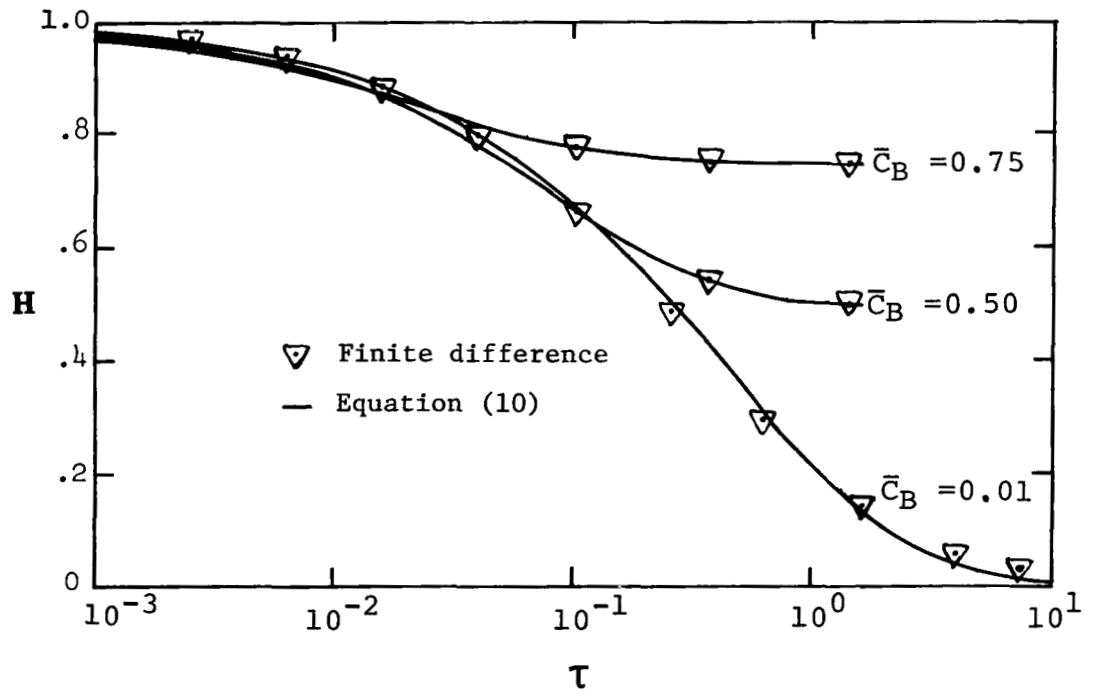
Figure 7.- Predicted homogenization values for specimens with cylindrical geometry and different $\bar{C}_B$ values.

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16. Abstract

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