Letters

The influence of inter-ion interaction upon the volume changes during sintering of binary alloys

A study of alloy sintering is complicated by several phenomena, namely vacancies in a diffusion zone, macroscopic and microscopic pore formation, dislocations etc. Investigations, based on phenomenological aspects of sintering have given some definite results, but according to one of the most competent scientists in the field, Samsonov [1], few results based upon the electronic theory of metals have been obtained.

In this note, we analyse the volume change during sintering of bi-component metallic systems. The discussion is based upon the inter-ion interaction between two components. The relation between the values of inter-ion interaction in the domain of the nearest neighbours, and the change of metal system dimensions during sintering are discussed. The basis of this analysis is electronic theory, which allows the problem to be treated at the level of elementary inter-ion interactions. We have chosen the inter-ion interaction because it corresponds to the energy required for the change of position of an atom in the crystal lattice, under conditions of constant volume. As the sintering process is caused by diffusion, we start with the logical hypothesis that the diffusion process, i. e. its rate, is proportional to the inverse value of the inter-ion interaction, since the diffusing ion has to overcome the interaction potential. Starting from this point it is suggested that the diffusion process will be the most rapid when the interaction is minimal, and vice versa.

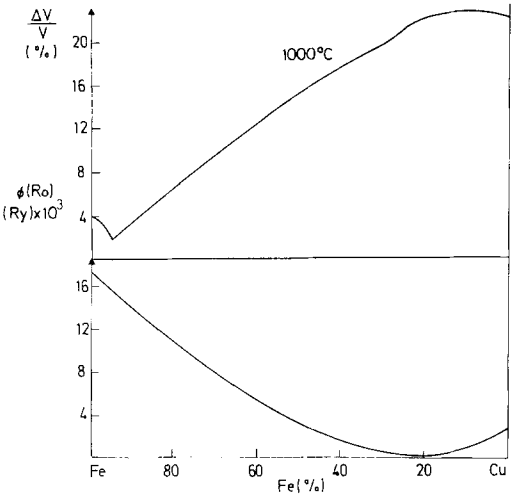

Figure 1 Correlations between the values $\phi(R_0)$ and changes of volume $(\Delta V/V)$ for the Fe–Cu system. Values for changes of volume are from [2].

It has been shown [2] that during the most rapid diffusion process, extreme changes of the system dimensions occur. Hence, one can expect these changes to correlate with the inter-ion interaction extremes in the domain of the nearest neighbours. We analyse the systems Cu–Ni, Cu–Fe, Cu–Co and Fe–Ni, in order to determine if the previous conclusion can be applied to real binary systems.

For the determination of the inter-ion interaction we use the asymptotic expression:

TABLE I Values of $\phi(R_0)$ for the Fe–Cu system

Fe (%)	$\phi(R_0)$ (Ry) × 10^{-3}
100	16.52
90	13.93
80	11.15
70	8.30
60	5.59
50	3.14
40	1.16
30	0.24
20	0.05
10	1.00
0	3.15

TABLE II Values of $\phi(R_0)$ for the Co–Cu system

Co (%)	$\phi(R_0)$ (Ry) × 10^{-3}
100	10.73
90	8.73
80	6.41
70	4.34
60	2.56
50	1.18
40	0.31
30	0.02
20	0.33
10	0.26
0	3.15

$$\phi(R) = \frac{9\pi Z^{*2}\,[V(2K_f)]^2}{E_f}\,\frac{\cos(2K_fR)}{(2K_fR)^3} \quad (1)$$

where Z^* is the valence number of a given metal, K_f is the Fermi momentum, E_f is the Fermi energy and $V(2K_f)$ is the form factor of the pseudopotential for electron–ion interaction in the metal, taken at the point $q = 2K_f$. Starting from the pseudopotential [3], the value, $V(2K_f)$ takes the following form:

$$V(2K_f) = \frac{a_1(Z - Z_0)}{2\pi} \sin[2\pi a_2 (Z - Z_0)] \exp(-a_3) \quad (2)$$

where Z is the atomic number of a given metal, Z_0 is the inert element atomic number that begins the period which includes the given Z, and the coefficients a_1, a_2 and a_3 are:

$a_1 = 0.2500$ Ry, $a_2 = 0.520$ Ry for short periods and the first half of long periods;
$a_1 = 0.0625$ Ry, $a_2 = 0.048$ Ry for the second half of long periods;
$a_3 = 0.3$ Ry for the first and second groups of the periodic system, and 0.4 Ry for all other groups.

The Expression 1 and 2 are used in connection with pseudoatomic approximation which assumes that the complex system is composed of pseudoatoms whose characteristics represent an average of real component characteristics [4].

The values of the ion–ion interaction potential at the position of the first deep minimum $\phi(R_0)$ for Cu–Fe, Cu–Co, Cu–Ni and Fe–Ni systems are given in Tables I to IV. Figs. 1 to 4 show a re-

TABLE III Values of $\phi(R_0)$ for the Ni–Cu system

Fe (%)	$\phi(R_0)$ (Ry) × 10^{-3}
100	16.52
90	15.06
80	13.48
70	11.79
60	10.02
50	8.28
40	6.61
30	4.99
20	3.51
10	2.24
0	1.19

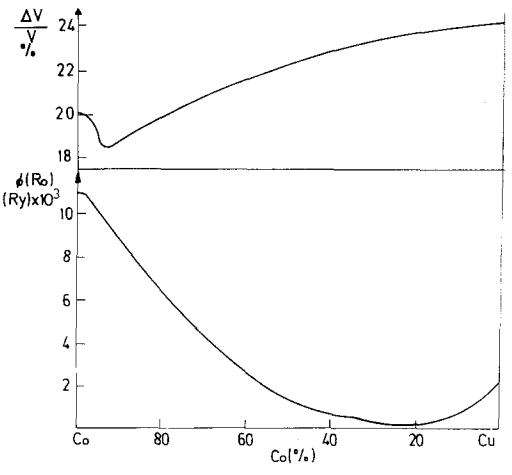

Figure 2 Correlation between the values $\phi(R_0)$ and changes of volume ($\Delta V/V$) for the Co–Cu system. Values for changes of volume are from [5].

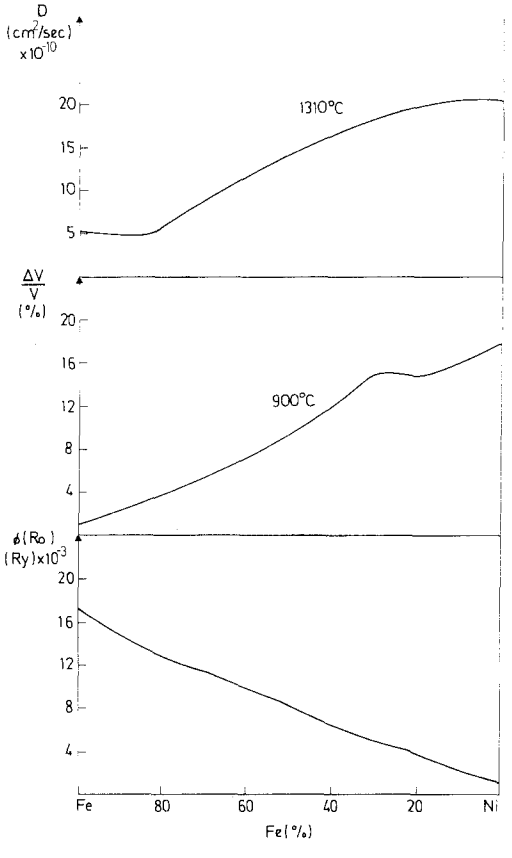

Figure 3 Correlations between the values $\phi(R_0)$ and changes of volume ($\Delta V/V$) and diffusion coefficient for the Fe–Ni. The values of changes of volume and diffusion coefficient are from [5].

TABLE IV Values of $\phi(R_0)$ for the Ni–Cu system

Ni (%)	$\phi(R_0)$ (Ry) × 10^{-3}
0	3.15
10	2.17
20	1.37
30	0.76
40	0.33
50	0.08
60	0.01
70	0.08
80	0.31
90	0.69
100	1.19

lation between the values $\phi(R_0)$ and the volume change during sintering process.

According to the results obtained, it can be seen that the volume changes correlate with the change of the inter-ion interaction in the domain of the nearest neighbours $[\phi(R_0)]$.

In conclusion, there is a correlation between inter-ion interaction of the nearest neighbours and dimension changes in the sintered system. According to the results from [5], the above correlation does not depend on time and sintering temperature. Since a similar analysis can be used for an n-component metallic system, it should be possible to predict the concentrations of different components which lead to the extreme volume changes during sintering.

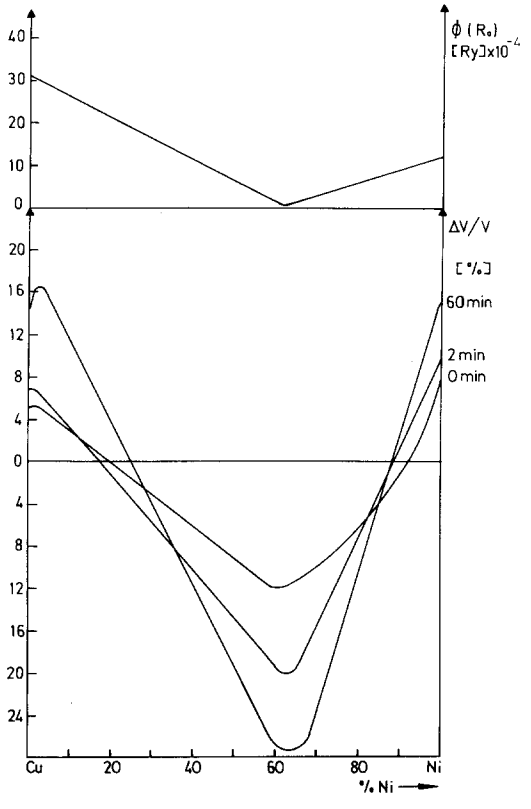

Figure 4 Correlations between the values $\phi(R_0)$ and volume $(\Delta V/V)$ for the Cu–Ni system. The values for the changes of volume are from [2].

References

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The crystal structure and space group of the mineral shortite

A study of minerals by Fahey [1] from mines in the Green River area of Sweetwater County in Wyoming, USA, indicated that the mineral shortite exhibited the pyroelectric effect. As part of a survey of pyroelectric materials samples of this material [2] from the West Vaco mine in the above region were obtained and examined for this effect. The physical appearance of the crystals was exactly as described and single crystal X-ray data confirmed the symmetry as orthorhombic, and the indexing of the faces as correct. Chemical