In practice, the heat transfer coefficient will be temperature dependent and will vary from stage to stage. The cooling rates calculated on the assumption of a constant value of $h$ can only represent the average cooling rate by virtue of $h$ obtained from isothermal freezing being intermediate to those prevalent in liquid and solid state cooling regimes [17].

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# *Influence of external magnetic and electric fields on sintering, structure and properties*

Diffusion processes occurring during sintering can be significantly altered by applied electric or magnetic fields, resulting in novel structures with unique properties. This paper summarizes recent theoretical work by the author on the influence of inhomogeneous temperature distributions arising during electrical sintering on diffusion behaviour, and on the sintering of magnetic materials. Studies by Hermel *et al.* [6] corroborate the theoretical ideas presented here on electric sintering, but the author is unaware of any experiments on the sintering of magnetic materials in a magnetic field with which to compare this aspect of this theory.

## *1. Influence of uneven temperature distribution on diffusion processes during Joule sintering*

The diffusion kinetics of macroscopic lattice defects is not enhanced either by passing direct current through a specimen or placing it in a uniform temperature gradient, *per se*. However, electric (Joule) heating can introduce a spacially varying temperature gradient within the specimen, and this can cause such diffusion. For instance, the temperature distribution, $T(r)$, in a wire under steady electric heating conditions is given by

$$T(r) = (\sigma\langle E\rangle^2/4\kappa)(R^2 - r^2) + T_0 \qquad (1)$$

where $\sigma$ is the electrical conductivity, $\kappa$ the thermal conductivity, $T_0$ the temperature of the surface of the wire, $\langle E\rangle$ the external homogeneous

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electric field, $R$ the radius of the wire, and $r$ the distance from the axis of the wire. Equation 1 indicates that the temperature at the axis is higher than that at the surface by several K, given $R = 0.05\,\text{cm}$, $\langle E\rangle = 0.3\,\text{V cm}^{-1}$ and selecting a typical value of $\sigma/\kappa$ for a metal. Such a temperature difference corresponds to an average temperature gradient of $\sim 50\,\text{K cm}^{-1}$, and can introduce steady state vacancy migration to or away from the axis of the wire, depending on the sign of the thermal diffusion ratio (Soret effect).

More importantly, since Joule heating results in spatially varying temperature gradients with a non-zero Laplacian, $\nabla^2 T = \sigma\langle E\rangle^2/\kappa$, an additional term is introduced into the expression for the rate of change in pore radius with time [1]. This term is significant because it can result in a marked increase (several orders of magnitude) in the rate of shrinkage of vacancy sources or sinks, such as dislocation loops and pores, for certain materials [2]. It must be emphasized that the additional driving force for void shrinkage is present only when $\nabla^2 T \neq 0$, a condition most readily realized by Joule heating.

Another important consequence of Joule heating is the reduction of surficial or "skin" sintering [3]. This harmful effect can be minimised by Joule heating since the driving force for diffusion acts uniformly throughout the bulk material. If Joule heating is steady (i.e. the current passed and the temperature of the sample are constant), then the temperature inhomogeneity arising due to Joule heating is maximized. During heating up, however, the additional driving force for diffusion is reduced by the factor

$$(\sigma\langle E\rangle^2 - c\,\partial T/\partial t)/(\sigma\langle E\rangle^2),$$

where $c$ is the specific heat of the solid.

The sign of the driving force for diffusion is determined by the sign of the thermal diffusion ratio $\tilde{J}_\text{T}$,† according to:

$$\mathbf{I}_\text{a} = (D/T)\tilde{J}_\text{T}\nabla T \qquad (2)$$

where $\mathbf{I}_\text{a}$ is the flux of atoms created solely by the temperature gradient, $\nabla T$, and $D$ is the diffusion coefficient. Joule heating will promote pore healing if $\tilde{J}_\text{T} > 0$, and impede it if $\tilde{J}_\text{T} < 0$ [2]. In fact, at sufficiently high power imputs $(\sigma\langle E\rangle^2)$, pores can even grow. It is observed experimentally that $\tilde{J}_\text{T}$ is different for different materials, e.g. for Cu, $\tilde{J}_\text{T} > 0$ whereas for Au, $\tilde{J}_\text{T} < 0$ [5]. Pore healing will, therefore, be enhanced in Cu and impede in Au.

## *2. Structure and properties of materials sintered by passage of an electric current (Joule heating)*

The diffusional driving forces derived from Joule heating do not depend on the type and size of pores [1]. Customarily, surface tension is the factor primarily involved in pore healing, and this is proportional to the curvature of the pore surface, increasing as the size of the pore decreases. For a fixed power input (fixed value of electric current) there is a specific pore size, $r_0$, such that for pores smaller than $r_0$ surface tension forces dominate, and for pores $> r_0$ in size, forces derived from Joule heating dominate [1]. For a pore of radius $r_0$, we have [6]

$$r_0 = 2\gamma c_\text{v}\kappa/\sigma\tilde{J}_\text{T}\langle E\rangle^2 kp^2 \qquad (3)$$

where $\gamma$ is the specific surface energy, $c_\text{v}$ is the equilibrium atomic vacancy concentration, $k$ is Boltzmann's constant, and $p$ is the mean free path of an excess vacancy. Values of $r_0$ range typically from fractions of a micron to several microns. For example, for Fe at $T = 1370\,\text{K}$, and given $\langle E\rangle = 0.2\,\text{V cm}^{-1}$ and $p = 2 \times 10^{-3}\,\text{cm}$, $r_0$ is $5 \times 10^{-4}$ cm [6]. If there are many pores in the sample, the annihilation of small pores supplies the vacancies for the growth of large ones [3]. However, if $\tilde{J}_\text{T} > 0$, large pores are themselves decreased in size by Joule heating, and so cannot act as sinks for vacancies emitted by the small pores. Consequently, the rate of annihilation of small pores is impeded. In short, one can draw the following qualitative conclusions from such considerations:

(1) the additional driving forces for diffusion resulting from Joule heating reduce the rate of decrease of the total number of pores, leading to a smaller average distance between pores;

(2) during conventional furnace sintering, small pores are annihilated and large ones remain. During Joule sintering, however, when $\tilde{J}_\text{T} > 0$, the annihilation of small pores is impeded and large pores $(> r_0)$ enhanced. This results in a broader distribution of pore sizes;

(3) average pore size increases during furnace sintering, and decreases during Joule sintering.

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† $\tilde{J}_\text{T}$ is proportional to the heat of transport parameter, $Q^*$, discussed by Shewmon [4].

These conclusions have been confirmed by experiments [6].

If $\tilde{J}_T < 0$, large pores ($> r_0$) grow during Joule sintering. This can lead to the development of unique structures which can significantly alter mechanical and physical properties, as described in detail in [6].

### *3. Novel features of diffusion processes during sintering of magnetic materials in a magnetic field*

Consider the distortion of the magnetic lines of force around a pore [7]. The presence of a spherical pore in a one-domain spherical magnetic solid with a constant direction of magnetic moment does not change the magnetic energy of the system. But if the pore elongates along the direction of the magnetic moment (pore volume, $v$, remaining constant), the distortion in the magnetic lines of force is reduced, and so is the magnetic energy of the system. However, one must also take into account the increase in energy of the system due to the increase in surface area of the elongated pore. Such considerations lead to the following conclusions:

(1) competition between magnetic energy decrease and surface energy increase determines the equilibrium ratio $(a/b)$ of the major axes of a pore of constant volume. This ratio increases as pore volume grows, such that if $\gamma = 10^3$ erg cm$^{-2}$ and $M^2 = 2 \times 10^6$ erg cm$^{-3}$, then the ratio $(a/b) \simeq 1.2$ when $v = 10^{-12}$ cm$^3$, but $(a/b) \simeq 3.4$ when $v = 10^{-9}$ cm$^3$ ($M$ is the magnetic moment of a unit volume of crystal);

(2) an increase of surface energy accompanying growth of a small pore prevails over the decrease in magnetic energy, while the opposite is true for a large pore. Thus, the dependence of the Gibbs free energy ($G$) of the system on the volume of a pore is not monotonic, but exhibits a maximum at $v = v_c$. (A typical value for $v_c$ is $\sim 10^{-9}$ cm$^3$). Thus, pores of $v < v_c$ tend to dissolve, and pores of $v > v_c$ tend to grow spontaneously, reducing $G$. At $v = v_0$, $G$ attains a value corresponding to $v = 0$, and decreases monotonically as $v$ becomes larger than $v_0$.

### *4. Structure and properties of magnetic materials sintered in a magnetic field*

The effects described should introduce particular pore-size distributions and pore orientations in magnetic materials sintered in a magnetic field. These, in turn, may give rise to peculiar and anisotropic mechanical and physical properties. Magnetic anisotropy, in particular, may be considerable [7, 8]. Even if all the pores are small and almost spherical, the magnetic anisotropy energy can reach values of order $\sim 10^3$ to $10^4$ erg cm$^{-3}$ at a porosity concentration of $\sim 1\%$, and in fact, pores can often be the major contributor to magnetic anisotropy in thin films and ceramics. These effects most probably may be achieved in Co and Co-based alloys, for which the Curie temperature (1100° C) and sintering temperatures (> 1000° C) are comparable. For materials having lower Curie temperatures, it may not be possible to realize the benefits of these effects.

In conclusion, the author recommends that further experiments be undertaken to more completely reveal the differences in properties of specimens produced by Joule sintering, and by sintering of magnetic ceramics in a magnetic field, from those of specimens produced by conventional furnace sintering.

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