Letters

Undercooling during atomization of VM300 maraging steel

During atomization of VM300 maraging steel in vacuum or in various atmospheres, such as argon, nitrogen or steam, it was found that a certain number of liquid droplets undercooled substantially prior to nucleation of the solid. This was established by examining the microstructure and distribution of solute within the as-solidified material. Spheroidal particles examined varied in diameter between 0.5 and 4.5 mm and were obtained by modifying processing variables during atomization.

The microstructure of a sphere that solidified at very low undercooling is normal dendritic (Fig. 1a). That of a sphere of approximately the same size, but which undercooled substantially is illustrated in Fig. 1b. In this case the dendritic structure appears disorganized with disconnected dendrite arms that exhibit high solute cores (light etching Fig. 2). Such structures were previously observed [1, 2] in iron-25 wt% nickel alloy and were attributed to a combination of undercooling, rapid cooling and intense convection.

Electron microprobe analysis was conducted along traverse paths analogous to that illustrated in Fig. 3, using a Materials Analysis Corporation microprobe with a take-off angle of 38.5°. The solidification structure was so fine that concentration measurements were conducted only at specific points along the chosen paths, such as the middle of the "light" dendrite arm core (A), the middle of the "dark" dendrite arm shell (B) and at some point within the interdendritic region. Elements analysed were nickel, cobalt and molybdenum. Their average concentrations in this steel were 18.5, 9.0 and 4.8 wt%, respectively. High solute dendrite arm cores (Fig. 3) were previously shown [1] to form during solidification of highly undercooled melts. The high concentration tends to level-off by diffusion in the solid after solidification, mainly because diffusion distances, $\overline{AB}$, are very short. Reasonably fast cooling is required for conserving the humps in the concentration profile. The average cooling rate of non-undercooled spherical particles with diameters between 0.5 and 4.5 mm has previously been found to vary between 10^2 and 10^3 sec^{-1}. These calculations were based on the assumption that heat-transfer during cooling is mainly by radiation and, to a lesser extent, by convection, and were confirmed by experimentally establishing the variation of dendrite arm spacing with cooling rate. For undercooled droplets, cooling rate after the end of recalescence [1] is expected to be somewhat higher than in non-undercooled droplets, because a large part of the latent heat of fusion has already been released during recalescence. Assuming a very short diffusion distance $l = \overline{AB} = 10^{-4}$ cm and a diffusivity of nickel in iron at 1200° C of $D = 10^{-10}$cm^2 sec^{-1} [3], the time necessary for extensive diffusion to take place would then be equal to $l^2/D = 100$ sec. Consider the droplet of largest size solidifying in steam at the lowest cooling rate of 10^{2}° sec^{-1}. For an alloy of liquidus temperature approximately equal to 1470°C significant diffusion in the solid is expected to take place down to about 900°, that is over a temperature interval of about 570° during about 6 sec. Even considering the approximations made, this time is too short for any extensive diffusion to take place. It can, of course, be argued that diffusion within the forming solid takes place also during recalescence between the equilibrium solidus temperature and the maximum recalescence temperature. The extend of this diffusion is expected to be limited, because of the very fast recalescence rates involved [1]. It can, therefore, be concluded that in atomized undercooled spheroids of the size range that was investigated herein the high solute cores will be only slightly modified by diffusion in the solid.

The percentage of spheres that undercooled is plotted versus sphere diameter or volume in Fig. 4. The observed decrease in probability of undercooling with increasing size may be attributed to the parallel increase in probability of existence of impurities adequate for nucleating the melt. This observation confirms previous results by Hollomon *et al* [4].

The width of the lump in the concentration profile was previously shown to increase with undercooling [1]. On the basis of this relationship a correlation was sought between amount of undercooling and sphere size, hence cooling

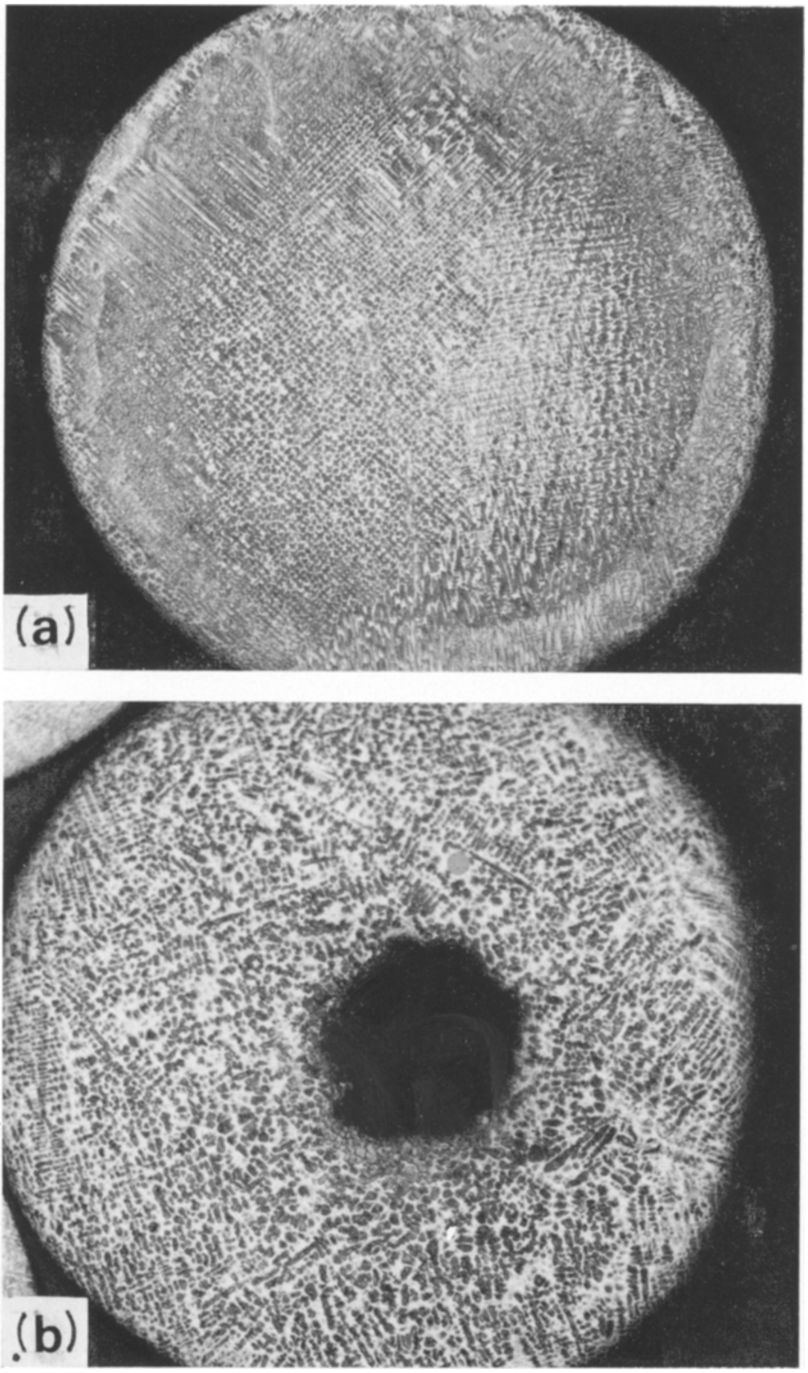

Figure 1 Photomicrographs of particles of VM300 maraging steel atomized in argon and etched with Rosenhain's reagent (a) Non-undercooled, (b) undercooled (× 100).

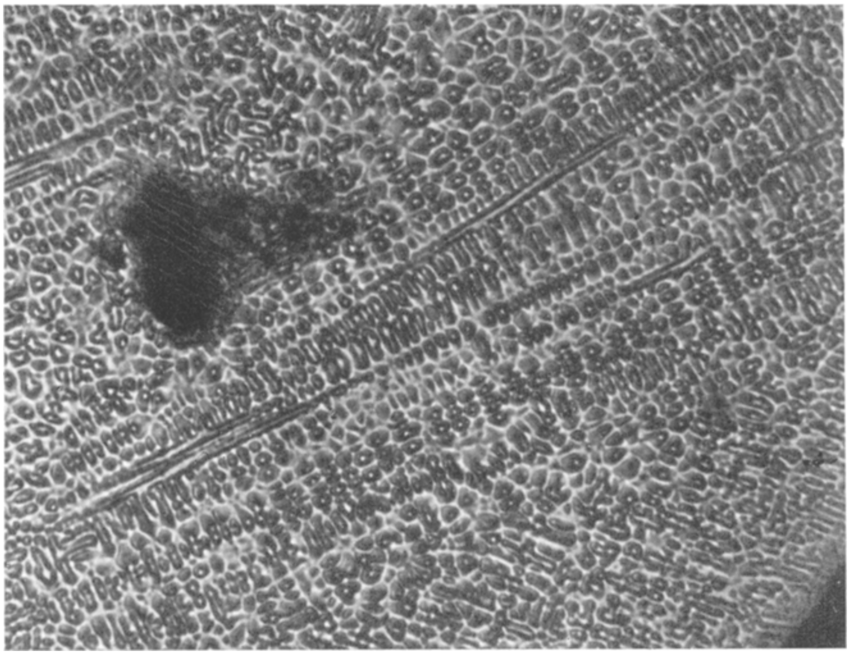

Figure 2 Photomicrograph of an undercooled particle of VM300 maraging steel atomized in argon (× 250).

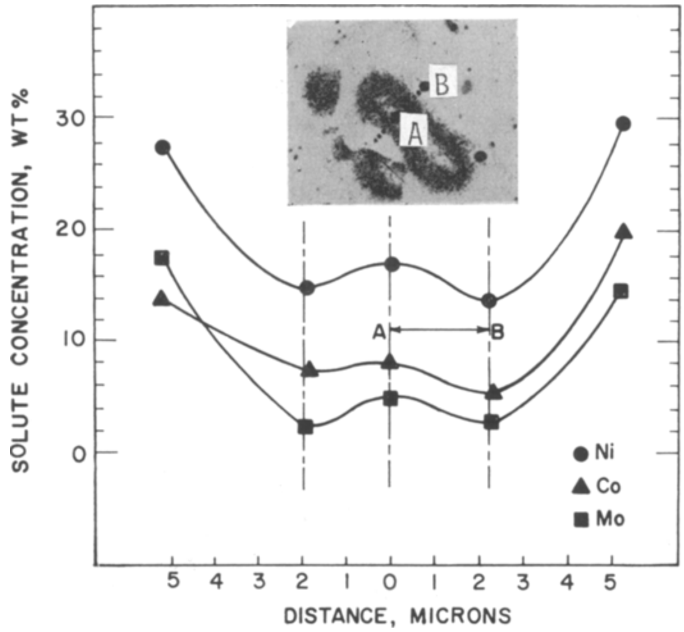

Figure 3 Distribution of Ni, Co and Mo concentrations measured at various specific points along the chosen microprobe path. Undercooled spherical particles in atomized VM300 maraging steel.

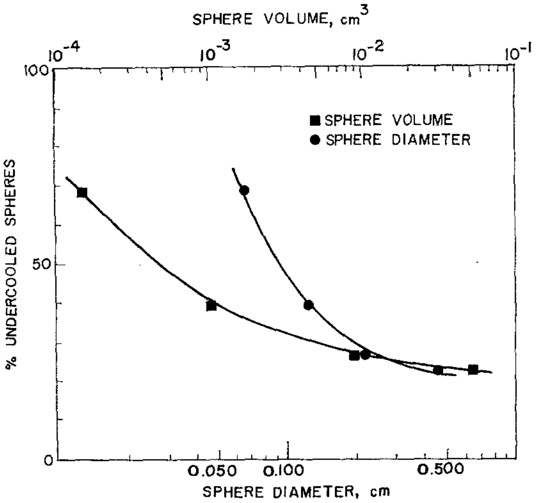

Figure 4 Per cent undercooled spheres versus sphere diameter or sphere volume, VM300 maraging steel atomized in argon.

rate. It has not been possible to establish a definite pattern. One of the basic difficulties in following this approach appeared to be the dependence on cooling rate or sphere size of the modification of the initial solute concentration profile, no matter how small.

Acknowledgement

The preparation of photomicrographs in Fig. 1 by Pascal Joly is gratefully acknowledged.

Reference

1. T. Z. KATTAMIS, *Z. Metallkde* **61** (1970) 856.
2. *Idem, Met. Trans.* **2** (1971) 2000.
3. T. Z. KATTAMIS and M. C. FLEMINGS, *Trans. Met. Soc. AIME* **233** (1965) 992.
4. J. H. HOLLOMON and D. TURNBULL, *Progress in Metals Physics* **4** (1953) 333.

Received and accepted 29 January 1974

T. Z. KATTAMIS
Department of Metallurgy,
University of Connecticut,
Storrs, Connecticut, USA
R. MEHRABIAN
Department of Metallurgy and Materials Science,
Massachusetts Institute of Technology,
Cambridge, Massachusetts, USA

Polymorphic transformation NaCl $\rightleftharpoons$ CsCl type: additional structural correspondence

The way in which the CsCl and NaCl structures interconvert in polymorphic MX compounds may be a guide to probable displacements in other structure changes since important structures such as fluorite are geometrically related to these. In investigations of CsCl and ammonium halides the orientation relation $(001)_{\mathrm{NaCl}} \parallel (001)_{\mathrm{CsCl}}$, $[110]_{\mathrm{NaCl}} \parallel [100]_{\mathrm{CsCl}}$, or an orientation 5° from it, has been observed among others [1-4]. This was the only orientation relation between NaCl- and CsCl-related forms of $\mathrm{RbNO_3}$, though there the geometry is complicated by an intermediate rhombohedral phase [5, 6]. The NaCl arrangement can be converted to the CsCl by a strain having the common $\langle 111 \rangle$ as principal axis [7, 8]. Martensite computations based on the $\langle 111 \rangle$ strain accounted for the other orientations, and the shape changes, at large supercooling, but not this orientation [9]. It could be obtained by

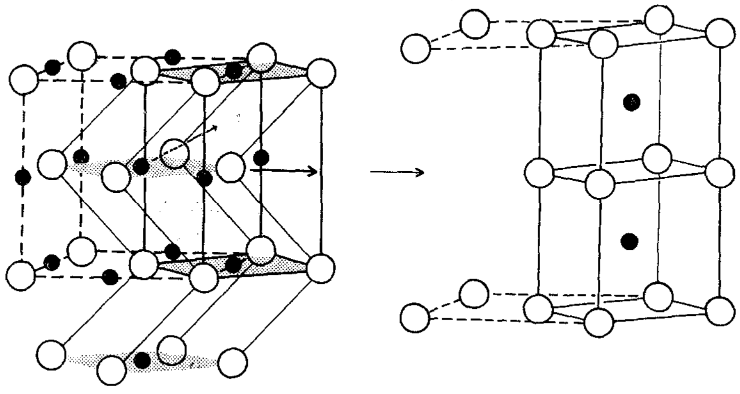

Figure 1 Conversion of the NaCl to the CsCl structure by "unfolding" of the packing and separation of cation and anion layers parallel to (001). Alternate (001) layers translate as indicated and the interlayer spacing of like ions increases. The outlined tetragonal cell becomes two CsCl cells.