

A different objective, involved the reaction of a manganese-nickel mixture of approximately 12:1 ratio by weight, respectively, with carbon. The plan of the test was to maintain the temperature at the relatively high value necessary for diamond formation through reaction of manganese and carbon (approximately 1500° C. Fig. 10), whereupon the manganese would be progressively removed from the solvent alloy by carbide formation. The residual manganese-nickel composition was expected to be displaced towards the relatively low melting eutectic at a 3:2 weight percent ratio (approximately 1000° C.). The effects looked for were both an improved solubility and transfer rate of carbon to the manganese reaction for prolific crystallization of high quality diamond. Since the temperature maintained was excessive for diamond formation from the low melting "reduced" Mn-Ni solvent, diamond growth was realized essentially from a simple Mn-C reaction. Crystals both of high purity and crystallinity have been obtained by use of this technique. The only included phase observed in a well performed experiment has been occasional recrystallized graphite, generally oriented along (111) planes. Figure 13 shows several diamond crystals representative of the better quality specimens obtained from (Mn, Ni)-C systems. Their size is approximately 0.3 mm.

Studies performed at constant pressure, with temperature and time variable, have provided additional support for the proposed growth mechanism. It has been observed generally that both the rate of growth and crystal size were subject to reasonable temperature control. For example, as previously mentioned, higher temperatures (within proper P-T bounds) usually yield a greater number of crystals but of smaller size. The situation is reversed at lower temperatures, primarily due to a lesser number of nucleation sites. In addition, crystallization, normally initially prolific, is observed to diminish rapidly. The total yield from a three minute experiment is not remarkably different from a nine minute one. New crystal formation is not rapid under steady state conditions. Following initial precipitation and crystallization, a system rapidly achieves equilibrium. Although new diamond formation essentially terminates, growth in crystal size is observed to occur through coalescence of existing crystals. The more fluid a chemical system and the longer the time, the more perfect is the coalescence. Coalescent growth also is a commonly observed phenomenon with the highly covalent material, SiC.

By lowering the temperature, precipitation can be reinitiated. By raising the temperature, supersaturation can be re-established with subsequent spontaneous precipitation. By cycling, within proper pressure-temperature limits for a given system, new growth can be rhythmically

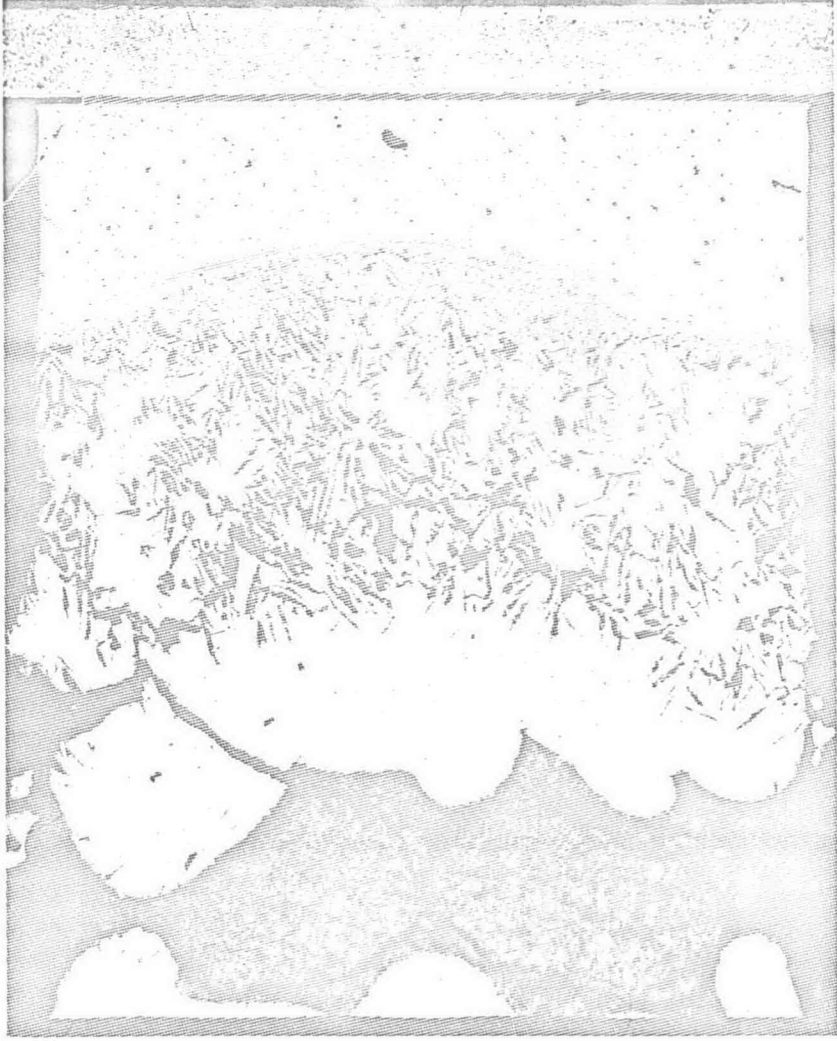


Fig. 12. A cross sectioned specimen showing a nickel-chromium-carbon reaction carried out at high pressure and temperature. The needle-like phase in the metallic area is  $\text{Cr}_3\text{C}_2$ . The mottled gray-black area at top center is unreacted graphite.

metallic solvents also may be achieved by the use of lower melting neutral elements such as copper; for example, systems such as Mn-Cu-C, or Ni-Cu-C.

An experiment performed utilizing a somewhat similar combination of solvents, namely a carbide former and non-carbide former, but directed to