Phase Equilibria and Capillary Properties in the Co-Mn-C System

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Keywords

Experimental method, phase equilibria, wettability, contact interaction, interfacial tension.

Abstract

Experimental studies of phase equilibria in the Co-Mn-C system and construction of the system melting diagram at atmospheric pressure have allowed a comprehensive investigation of capillary phenomena at the growth medium-carbon material interface that occur due to variations of both the liquid phase composition and melting temperature (along the solid-liquid equilibrium line).

It was shown, that cobalt melts containing 10-14 at% Mn might be recommended as growth media for diamond synthesis. Along with the relatively low p,T-parameters, the introduction of manganese in such quantities provide optimal synthesis conditions, i.e. the lowest energy at the crystal - growth medium interface with a rather high solubility of carbon in the melt.

Introduction

To examine the nucleation, crystallization of alloys and crystal growth processes, to know phase diagrams (composition range where the crystallization occurs) [1], and properties of interface between the precipitating phase and crystallization medium is important. Certain fields between liquidus and solidus of the phase diagram are characterized by their own dependencies of the wetting angles (θ), adhesion work (W_a) and interface tension (σ_{sl}) on temperature and equilibrium composition. For example, primarily crystallizing phases are wetted differently by eutectic liquid [2]. The fact determines to a large extent the solid phase nucleation and crystal growth, the shape [3-5] and distribution of grains of the precipitating solid phase, structure of castings, type and structure of eutectic colonies. For diamond crystallization from a metal-carbon melt, the growth media should have a sufficiently high carbon solubility in a melt and relatively low parameters (pressure and temperature) for its production in addition to the low values of interface energy at the crystal-growth media interface

In the present work, the phase equilibria in the Co-Mn-C system have been studied experimentally; the melting diagram of the system has been constructed at atmospheric pressure, graphite wettability with Co-C, Co-Mn, Co-Mn-C melts and contact phenomena at the graphite-metal melts interface have been examined, optimal temperature-concentration conditions for diamond growth from a given growth medium have been found.

Experimental

The graphite wettability with a metal melt was measured by the sessile-drop method using the equipment. described in [6] During the

experiments, the alloys and graphite substrates were heated separately in a vacuum of 1×10^{-3} Pa and brought into the contact as a given temperature was attained. The structure of contact interaction zones was examined by metallographic and electron probe analyses.

Results

The graphite wettability with Co-Mn melts (Fig. 1a) is characterized by smooth reduction with increasing manganese content.

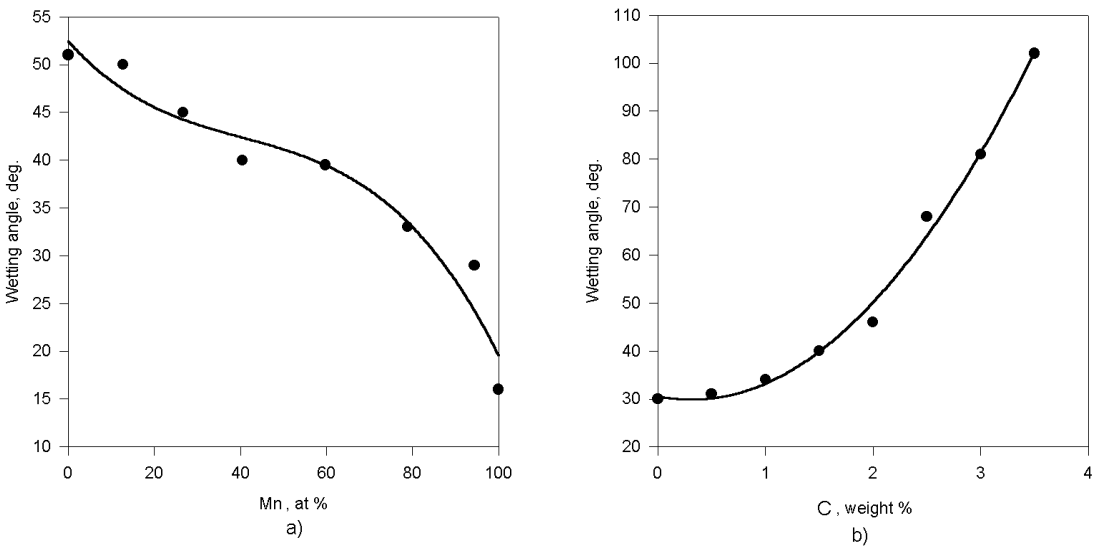

Fig. 1. Isotherms of graphite wettability with Co-Mn (a) and Co-C (b) melts at 1820 K.

Our studies of graphite wettability with the pure cobalt melt [7,8] have shown that wetting angle is 30 deg., practically doesn't change in the 1570-1820 K temperature range and is independent of the holding time at the experimental temperature. At 1820 K, the liquid cobalt spreads over graphite surface at a rate of about 10^{-2} c [9.] With increasing a carbon content of a cobalt melt, the wetting angle increases up to 101 deg. (Fig.1b). Maintaining such melts in the contact with graphite does not lead to the

accumulation of a drop. Drops keep their stable shape. The angles of graphite wetting with cobalt melts most heavily depend on carbon content in melts, that contain carbon in amounts approaching to the saturation (the fields where a system slightly deviates from the equilibrium state).

Graphite wettability with Co-Mn-C melts and contact interaction in this system were studied on the alloys, whose composition and heating temperature were determined from the Co-Mn-C melting diagram. Analysis of the constructed liquidus projection for the Co-Mn-C system has shown that the temperature of stable binary equilibrium carbon with liquid is rather low over a wide range of concentrations (from $x_{Co}/x_{Mn} = 2$ to $x_{Co}/x_{Mn} = 0,5$) (Fig.2). At lower temperatures, carbide crystallization occurs, which is a competitive process with diamond obtaining at high pressures as the dissolved carbon is consumed in such a process.

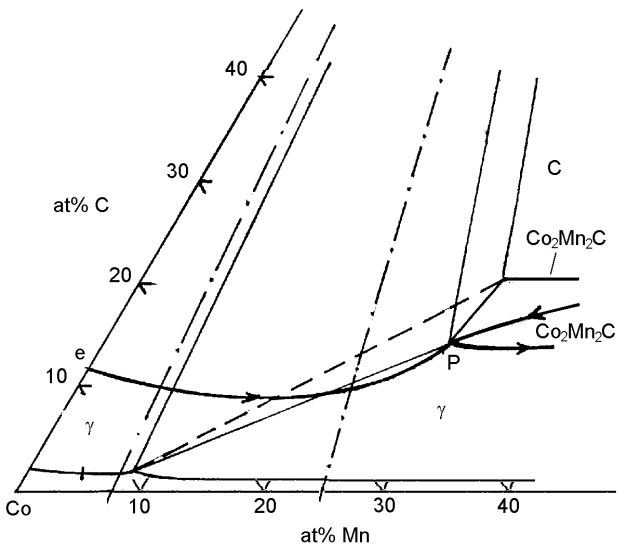

Fig. 2. Liquidus surface projection of the Co-Mn-C diagram in cobalt rich region.

To avoid the described phenomena, cobalt and manganese alloys having up to 30 at% Mn are used as solvents for diamond synthesis. In this

composition field, where a considerable temperature decrease is observed along the univariant eutectic L ⇆ γ + C line, the wettability and contact interaction between graphite and Co-Mn-C melts have been examined to define the optimal composition of a growth medium for diamond obtaining. The optimal composition should be characterized by minimum values of interface energy at the melt-graphite (diamond) interface, which results in decreasing critical size of diamond nuclei [3].

The Co-rich part of the Co-Mn-C diagram is shown in Fig.2. The polythermal sections and plane of invariant peritectic equilibrium L+C ⇆ γ + Co_2Mn_2C are shown too. The alloy concentrations for the wettability studies were chosen along the eP line of the univariant graphite eutectic L ⇆ γ + C at 5, 10, 15 and 17 at% Mn, that correspond to 9-11 at% C. The superheating value with respect to the liquidus temperature was kept constant (80K) for all alloys. Alloys compositions and eutectic temperatures are given in the Table 1.

Table 1. Alloys compositions and eutectic temperatures of the Co-Mn-C system

Marks in the diagram	Compositions, at %			Eutectic temperature, K
	Co	Mn	C	L⇆ C + γ
A	85,5	5	9,5	1500
B	81	10	9	1420
C	75	15	10	1400
D	71	17	11	1390

Our results show (Fig.3), that concentration dependencies of graphite wettability with Co-Mn-C melts as well as the carbon content of the eutectic liquid have their minimums around 10-14 at% Mn. The found mode of capillary variations of the above contact system points to the peculiarities of interactions between all the components of the melt and with the solid phase (graphite) and is, evidently, determined by the change of both volume and surface properties, in particular, adhesive and thermodynamic activities of melt components. So, positive effect of manganese on wettability is observed up to 12 at%, a higher manganese concentration leads to the decrease in adhesive activity (Fig.3).

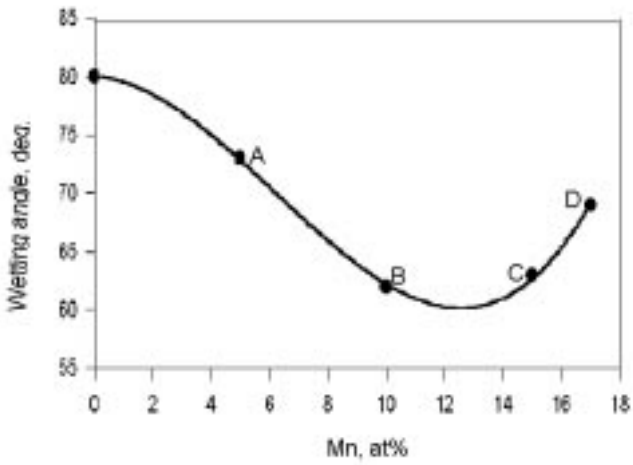

Fig. 3. Graphite wettability with Co-Mn-C melts.

Correlation between the wettability variation and phase equilibria in the Co-Mn-C contact system is confirmed by polythermic sections constructed from experimental DTA data. Polythermic sections (Fig.4) pass through the apex of the concentration triangle and cross the Co-Mn side of the Co-Mn-C diagram at the cobalt-manganese ratio of 92:8 (section 1) or 75:25 (section 2). These ratios were chosen from the results of wettability

study so that the constructed sections passed through the composition of alloys exhibiting the different trends (decreasing or increasing) in wetting angles variation and therefore in increasing the interface energy at the diamond-growth medium interface. Both sections pass in the fields of graphite and γ-phase primary crystallization. The second section intersects the L + C ⇆ Co_2Mn_2C invariant peritectic equilibrium plane. The alloys of the first section consist of two solid phases: graphite and solid γ-solution on the basis of fcc cobalt that dissolves a small (1.5-2 at%) amount of carbon and all manganese content of the alloy. A third phase - double carbide Co_2Mn_2C - appears in the alloys of the second section, because of this manganese is redistributed between the γ-phase and Co_2Mn_2C carbide. In the alloys of the first section, the L ⇆ γ +G graphite eutectic melts between 1485 and 1520 K. The melting and crystallization of the alloys of the second section are of a more complex mode due to the more complicated phase equilibria (Fig.4).

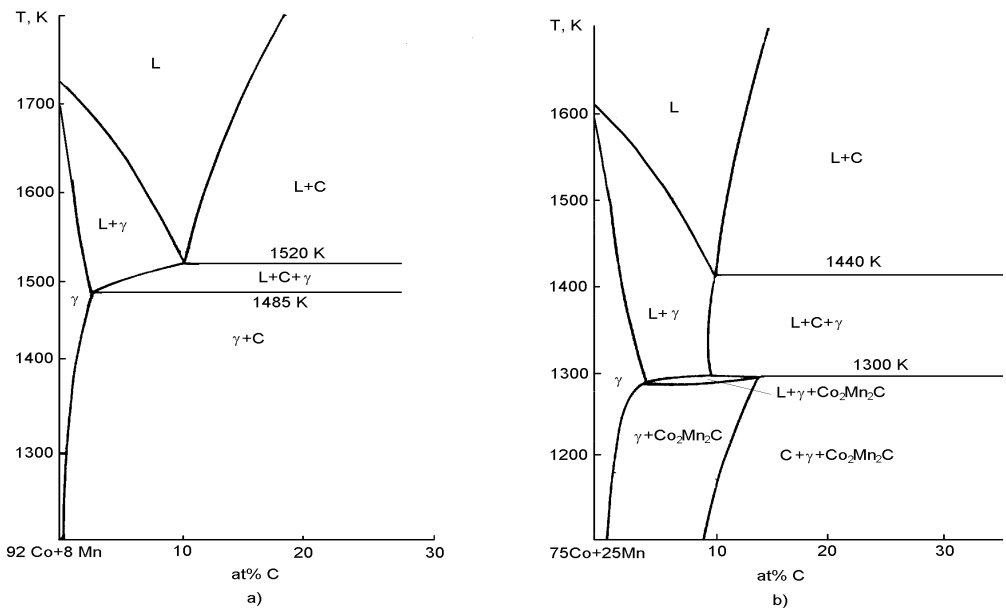

Fig. 4. Polythermic sections of the Co-Mn-C diagram, passing through carbon apex and compositions of the Co-Mn system.

The structures of contact interaction zones of graphite with liquid cobalt and manganese as well as with Co-Mn and Co-Mn-C melts have been studied. The structure of the graphite - pure liquid cobalt interaction zone is eutectic. At the contact zone of graphite with pure liquid manganese, carbide Mn_7C_3 crystals prevail, that in some places are surrounded by thin interlayers of another carbide, perhaps Mn_5C_2. Contact interactions of graphite with carbon-free Co-Mn melts were studied at 16; 26.4; 39.6; 60.6 at% Mn. With increasing manganese content, the Co_2Mn_2C and Mn_7C_3 carbides appear in contact zones between graphite and melts, the amount of the γ-phase decreases and the β-phase (a solid solution on the basis of β-manganese) forms. The structures of contact interaction zones between graphite and carbon-containing and carbon-free melts of the Co-Mn-C system are similar at the equal manganese concentrations (up to 17 at%) in the initial alloys.

Analysis of our findings on graphite wettability with Co-Mn-C melts permits some generalizations to be made. For carbon-free melts, when the maximal nonequilibrium conditions for the contact between a liquid and a solid phase are realized and the process of carbon dissolution from a substrate to the liquid metal occurs, the wetting angles are rather low. With melt saturation by carbon no matter whether the melt contains one or two metals active to a graphite surface, the wettability is impaired. Under the equilibrium contact conditions, wetting angles are considerably larger than those under the nonequilibrium ones.

Conclusion

Cobalt melts containing 10-14 at% Mn might be recommended as growth media for diamond synthesis since the introduction of manganese in such quantities ensures the lowest interfacial energy, i.e. low work of

diamond nucleation at a sufficiently high solubility of carbon in the melt and relatively low parameters of diamond synthesis.

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