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Roles of Unstable Chemical Species and Non-Equilibrium Reaction Routes on Properties of Reaction Product—A Review

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Chemical species might be held in a state being away from equilibrium state, at least temporarily, as represented by non-graphitic carbon and gaseous ammonia NH_3 with suppressed extent of dissociation by flowing. Such chemical species X in unstable state would possess chemical activity $a(X)$ considerably higher than that of the same element in equilibrium (reference) state. In case of carbon, $a(C)$ of amorphous carbon is higher than that of graphite (equilibrium state of C; $a(C) = 1$). Thus, when metal M is reacted with excess C, carbon content x' in carbide $MC_{x'}$ in equilibrium with amorphous carbon becomes higher than x in MC_x in equilibrium with graphite. In case of uranium carbo-nitride UC_xN_{1-x} in equilibrium with excess free C under given conditions of temperature T and N_2 gas partial pressure $p(N_2)$, x' in $UC_{x'}N_{1-x'}$ in equilibrium with amorphous carbon was experimentally demonstrated to be higher than x in UC_xN_{1-x} in equilibrium with graphite. Gaseous ammonia NH_3 with suppressed extent of dissociation by flowing would yield very high nitrogen activity $a(N)$ and modestly high hydrogen activity $a(H)$ while NH_3 dissociated to N_2 and H_2 to reach equilibrium state in closed reaction chamber would yield $a(N)$ and $a(H)$ to be represented by respective partial pressures, $p(N_2)^{1/2}$ and $p(H_2)^{1/2}$, in the gas phase. Synthesis of mono-nitride MoN of Mo in N_2 gas was reported to be impossible even at high pressure up to 300 atm in autoclave but MoN co-existing with sub-nitride Mo_2N might be synthesized in flowing NH_3 gas at normal pressure. As such, unstable chemical species might allow us to synthesize novel reaction product that cannot be prepared by using stable chemical species alone in the reactant. However, special care must be taken in usage of unstable chemical species. For example, in case of non-graphitic carbon, graphitization might proceed with considerably fast rate when the reaction temperature is set to be well above 2000 K and thence no effect of high $a(C)$ might be gained at reaction temperature exceeding 2000 K. On the other hand, in case of flowing NH_3 gas, extent α of dissociation of NH_3 gas would depend on the position along the flow path of NH_3 gas stream (i.e., α tends to rise inevitably on going from the up-stream side to the down-stream side) as well as on the NH_3 gas flow rate (i.e., α at specific position in the flow path tends to rise with diminishing NH_3 gas flow rate). On the other hand, rapid solidification processing with cooling rate reaching to 10^6 K/s has been employed for refinement of microstructure of alloys and for extension of solubility limit as well as for formation of amorphous phases. Rapid solidification is considered as ultra-fast quenching process of high temperature micro structure, or more precisely, retention of atomistic configuration in molten state of multi-component system through extraction of heat with very high rate to inhibit atom diffusion processes to reach inherent equilibrium state defined uniquely as functions of temperature T and alloy composition. On the other hand, under certain mode of operation of solar furnace using concentrated solar beam as the reaction heat source, rapid heating to reach reaction temperature around 2000 K from ambient temperature within order of a second or even less is realized. During carbide synthesis from tungsten (W) under such operation mode of solar furnace, the authors detected evidence of formation of W_mC_n phases that did not correspond to the phase anticipated by referring to available equilibrium binary W–C phase diagram at the processing temperature. This experimental evidence is tentatively appreciated in terms of small energetic differences among W_mC_n phases with varying m/n ratios. That is, once certain W_mC_n phase is formed during rapid heating of W/C powder mixture, the formed phase would remain stable at the processing temperature T even if it is not the genuine equilibrium phase at T without being transformed to the genuine equilibrium phase at the specified T due to smallness of driving force for the phase transformation

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