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Thermal decomposition of δ-MoN and ε-Fe_2N synthesized under concentrated solar radiation in NH_3 gas stream

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ABSTRACT

Decomposition temperatures of δ-MoN and ε-Fe_2N synthesized with flowing NH_3 gas under concentrated solar radiation heating were evaluated by Differential Scanning Calorimetry (DSC) in Argon (Ar) gas environment. The measured decomposition temperature of δ-MoN and ε-Fe_2N were dependent on the solar synthesis conditions, particularly either NH_3 or N_2 gas flow rate at temperature. Sample containing δ-MoN showed two exothermic peaks around 680 and 900 °C, attributed to the reactions of δ-phase into γ-single-phase and (γ+β)-two-phase Mo_2N, respectively, attributed to the dissociation reaction of δ-phase into γ-single phase and the dissociation reaction of γ-phase into metallic M saturated with N, respectively. Decomposition of ε-Fe_2N took place into γ'-Fe_4N in two steps occurring at 606 and 660 °C, respectively. When N_2 instead of ammonia (NH_3) gas was used, complete dissociation of γ'-Fe_4N into Fe took place at around 610 °C. Full decomposition of γ'-Fe_4N into metallic α-Fe(N) was corroborated by X-ray diffraction (XRD) analysis.

1. Introduction

Transition metal nitrides belong to the family of "interstitial compounds" known for their face-centered cubic (*fcc*) or hexagonal close-packed (*hcp*) metal lattices where nitrogen atoms are randomly distributed on the interstitial sites. Because of the unique performance characteristics of the interstitial compounds in the binary Fe–N and Mo–N systems, several authors attempted syntheses of specific nitride phases of Fe and Mo due to their exceptional hardness, high melting point, excellent corrosion, and wear resistance [1,2]. Additionally, the ferromagnetic iron nitrides' tuneable magnetic properties, attributed to $Fe_{16}N_2$ [3] and Fe_4N [4], make them suitable for magnetic data and information storage. Moreover, molybdenum nitride catalysts are regarded as being suitable for the hydro-denitrogenation (HDN) and hydro-desulfurization (HDS) of compounds such as benzothiophene, and benzofuran [5,6]. Hargreaves [7] reviewed the application of molybdenum nitrides in heterogeneous catalysis. He concluded that exciting developments can be anticipated, providing that synthesis of such compounds in large batches is realized.

It is well known that δ−MoN is an unstable compound, and it is difficult to synthesize using molecular nitrogen gas even at pressures as high as 30.4 MPa (300 atm) [8]. Although it was originally thought that molybdenum did not form nitrides at atmospheric pressure, Hägg [9] was able to obtain nitrides by heating Mo-powder in dry ammonia. He produced compounds varying in nitrogen content in the 400–700 °C temperature range, which were identified by XRD analysis as β-phase--stable only above 600 °C and containing about 28 at.% N, with the metal atoms forming a face-centered tetragonal lattice, γ-phase stable at T below 700 °C, faced-centered cubic, in which nitrogen atoms occupy octahedral sites in the region of 33% at.% N_2, and δ-phase at 800 °C, hexagonal, in the region of 50 at.% N_2, being isomorphous with MoC. XRD diffraction lines assigned to MoN became apparent in addition to Mo_2N after 10 h under NH_3 flow at 700 °C. With increasing reaction time from 10 to 20 h, Mo_2N (111) diffraction line intensity became higher than MoN (100) one. The opposite occurred after 60 h reaction period. At 725 °C, MoN did not form even under flowing NH_3 owing to its dissociation into Mo_2N and N_2 gas. These findings were later confirmed by Schönberg [10], who showed that δ-MoN could indeed be obtained in a constant stream of dry ammonia, up to 725 °C for a few hours, because of the remarkably high nitrogen potential of flowing NH_3. He found that

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