Note

Inhibition of Grain and Precipitate Growth of AISI M2 Type Tool Steel Powders by Low-temperature Nitriding Using Flowing Ammonia Gas

1. Introduction

Flowing gaseous ammonia (NH_3) is often employed as nitriding agent for metals and alloys that are difficult to be nitrided by gaseous N_2 (e.g. Refs. 1)–5)). Known merits of using NH_3 gas as nitriding agent are; (1) comparatively low reaction temperature T ; (2) fast rate of reaction; (3) possibility of forming higher nitride which would be difficult to prepare through reaction with N_2 gas (even with high pressure up to around 300 atm).

In recent thermodynamic analysis, Katsura^{6–11)} showed that nitrogen activity $a(\text{N})$ and hydrogen activity $a(\text{H})$ of flowing NH_3 gas might be expressed as functions of temperature T and extent α of dissociation of NH_3 gas and concluded that high $a(\text{N})$ effect gained by use of NH_3 gas as nitriding agent is ascribable to realisation of condition under which unstable NH_3 molecules are present in the gas phase.

In the present work, AISI M2 type high speed tool steel powders were subjected to low temperature nitriding under flowing NH_3 gas and they were then sintered in vacuum. The aim of nitriding the steel powders under NH_3 gas flow at low temperature was to retain the refined microstructure of the as-atomised powders. Virtually all interstitial N atoms introduced by the initial nitriding process were lost during the sintering process but the obtained microstructure of the sintered body was appreciably different from that of the reference sintered specimen prepared from the as-received steel powders without being nitrided. Possible causes leading to the observed microstructure difference between the nitrided and non-nitrided AISI M2 steel powders after sintering are discussed in this communication.

2. Experimental

Water atomised and then annealed AISI M2 steel powders (see Table 1 for composition) were nitrided under flow of NH_3 gas (flow rate was set to yield gas line velocity *ca.* 6 cm/min in the reaction tube) in the range of temperature, 500–600°C, for duration between 1 and 5 h in the alumina tube furnace. In this nitriding operation undertaken in alumina tube furnace, heating

was done in flowing NH_3 gas. This was to ensure removal of surface passive layer during the heating by action of NH_3 . As reported earlier,⁵⁾ when the specimen heating was not done in flowing NH_3 gas in this type of nitriding process, passive film remained on the steel surface and the desired nitriding reaction at the reaction temperature was very much retarded. On the other hand, furnace cooling after the nitriding reaction was done in flowing N_2 gas. This was to avoid undesired removal of nitrogen from the nitrided steel powder surface by action of NH_3 as the high $a(\text{H})$ medium.

N level of nitrided powders was determined using N and O simultaneous analyser model TC-436 of LECO.

The nitrided powders, and the reference as-received powders, were compacted into pellet with addition of 0.2 mass% graphite and sintered in vacuum at 1240°C.

3. Results and Discussion

As summarised in Table 2, N content in M2 steel powders rose from initial 0.027 mass% to above 5 mass% after 1 h nitriding at 550°C under NH_3 flow or after 3 h nitriding at 500°C. This level of N is close to N/Fe atomic ratio 1/4 but it did not seem to mean that formation of Fe_4N (γ' -phase) took place judging from XRD (X-ray diffraction) analysis that showed well developed (101) peak of hcp (hexagonal close packed)

Table 2. N content (in mass%) in nitrided M2 steel powders.

t (h)	T (°C)		
	500	550	600
1	—	5.6	—
3	5.1	9.8	10.2
5	—	10.4	—

Fig. 1. XRD patterns of the M2 powder specimens nitrided at 550°C.
(1) as-received M2 powders,
(2) after 1 h nitriding,
(3) after 3 h nitriding.

Table 1. Nominal composition of AISI M2 tool steel.

Element	C	N	O	Cr	Mo	W	V	Fe
mass%	0.91	0.027	0.058	4.06	4.60	5.80	1.76	bal.

ϵ -phase nearby (110) peak of bcc (body centred cubic) α -phase (Fig. 1). In XRD pattern of specimens with N level around 10 mass% (nitrided at 550 or 600°C for more than 3 h), (101) peak of hcp ϵ -phase developed further and (110) peak of bcc α -phase became indiscernible. Thus, in the examined range of nitriding conditions, bcc steel matrix seemed to be converted directly to hcp matrix without being passing through intermediate fcc (face centred cubic) γ' phase.

According to the LECO analysis, oxygen levels in nitrided powder specimens were in the range between 2 000 and 3 500 ppm.

Figure 2 compares appearance of the partially nitrided M2 powder (a) and that of the fully nitrided M2 powder (b). It is seen clearly that the nitrided steel matrix became more resistant against the nital etching and that the growth of the carbide precipitates was well suppressed during the nitriding.

Figure 3 compares appearances of sintered specimens. N content in these specimens was reduced down to level no more than 0.01 mass%. Grain and carbide size are larger for the sintered as-received powders (a) than for the sintered nitrided powders (b) and (c). The specimen (c) started from powders with *ca.* 10 mass% N was rather porous. This indicates that an incompletely nitrided structure (*e.g.* specimen (b) with *ca.* 5 mass% N) is preferable for obtaining a pore-free specimen by vacuum sintering to fully nitrided ϵ -phase.

Figure 4 compares SEM appearances of the sintered specimens; distribution patterns of precipitates are clearly seen herein. Coarse rather edgy precipitates observed in (a) and (b) are identified to be M_6C type

carbide. This type of carbide precipitates seemed to agglomerate on grain boundaries in specimens, (a) and (b). In contrast, coarse precipitate like this was non-existent in specimen (c) which was prepared by sintering of the fully nitrided ϵ -phase powders.

While much further research effort would be desired to be spent in order to elucidate processes taking place during sintering of highly nitrided steel powders, it seems certain that grain and precipitate growth is effectively inhibited on sintering of the M2 powders when the fully nitrided ϵ -phase powders of M2 steel are employed as the starting material and probable mechanism leading to such microstructural refinement for M2 sintering body prepared from highly nitrided powders must be interpreted in terms of inhibited diffusion of substitutional alloying elements, Cr, Mo, W and V, in the M2 steel specimen nitrided to hcp ϵ -phase.

Affinity of substitutional alloying elements like Cr, Mo, W and V in steel lattice to C and N is known to be stronger than that of Fe and, as shown in earlier statistical thermodynamic analyses for $Fe_{1-y}M_yN_x$,¹²⁻¹⁴ these substitutional atoms would tend to form cluster to be represented by Fe_3M or Fe_4M_2 surrounding N atom occupying an O-site (octahedral interstitial site). With reference to this information, suppressed diffusion

Fig. 2. Cross sectional appearances of powders nitrided at 550°C under NH_3 flow (optical micrograph; etched in 5% nital solution).
(a) 5.6 mass% N; 1 h nitriding
(b) 10.4 mass% N; 5 h nitriding.

Fig. 3. Appearances of specimens sintered in vacuum at 1 240°C for 1 h (optical micrograph; etched in 5% nital solution); starting materials were (a) as-received M2 steel powders, (b) powders nitrided at 550°C for 1 h and (c) powders nitrided at 550°C for 5 h.

Fig. 4. SEM appearances of specimens sintered in vacuum at 1240°C for 1 h (etched in 5% nital solution) showing distinctive conditions of precipitates; starting materials were (a) as-received M2 steel powders, (b) powders nitrided at 550°C for 1 h and (c) powders nitrided at 550°C for 5 h.

of substitutional elements, Cr, Mo, W and V in the nitrided steel lattice must be ascribable to the reduced mobility of these substitutional elements being fixed by the N atoms in the interstitial sites of the steel matrix.

4. Conclusions

Following conclusions were drawn from the present work.

(1) Ferritic M2 steel powders are fully nitrided to hcp ϵ -phase possessing composition close to Fe_2N under flow of NH_3 gas within 3 h in the range of temperature between 550 and 600°C.

(2) Specimen prepared from cold-pressed pellet of such fully nitrided powders by sintering at 1240°C in vacuum for 1 h was rather porous while porosity of the sintered body prepared from cold-pressed pellet of partially nitrided powders (a mixture of α -phase and ϵ -phase) was comparable to that of the reference speci-

men prepared from cold-pressed pellet of the as-received M2 steel powders.

(3) Size of precipitates in the sintered specimen prepared from the fully nitrided powders was very fine and distribution of precipitate particles was homogeneous while coarse M_6C type precipitates along grain boundaries were observed in the sintered specimen prepared from the partially nitrided powders as well as in the reference specimen prepared from the as-received M2 powders.

(4) While retention of N atoms introduced into matrix of M2 steel powders by low-temperature nitriding using flowing NH_3 gas is not possible after the sintering process, microstructure refinement effect is gained. Insertion of such nitriding process must be of pragmatic help to inhibit undesired grain and precipitate growth for some type of alloys.

(5) Steel powders subjected to the low-temperature nitriding under flowing NH_3 gas could be used as starting material for production of porous steel components.

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