Studies on Microstructural Phenomena Caused by Diffusion in Sintered Materials

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As microstructural phenomena caused by atomic diffusion in sintered materials, there are the following: (1) sintering, (2) grain growth, (3) alloying or generation of compound, (4) generation of peculiar surface layer in sintered compact, etc. The studies of the present author and co-workers on these phenomena will be introduced.

(1) Sintering: Proposal of Hypothesis "Equilibrium Gas Pressure" for Incomplete Sintering Densification of Compact[1]

The relative density of green compact of fine metal powder with size of 5~15 μm for MIM (Metal Injection Molding) is about 60%, and the compact easily densifies up to about 95% of theoretical density by sintering. The relative density, however, generally saturates near 95~98%. Such incomplete densification could not be explained by well-known theory "Separation of grain boundaries from closed pores". Then, we proposed the following new hypothesis "Equilibrium gas pressure", based on thermodynamics.

(i) Gases such as H_2O or CO generated by the reduction reaction of residual oxide with sintering atmosphere H_2 or impurity carbon in sintered compact is entrapped in closed pores.

(ii) If the equilibrium pressure of such entrapped gases is higher than the surface stress of closed pore ($\sigma = 2\gamma/r$. γ: surface tension, r: radius of closed pore), i.e., the driving force for densification, the densification of the compact becomes incomplete, and vice versa.

For example, the equilibrium pressure (P_{CO}) of CO entrapped gas in Fe compact containing C and O is expressed by the following equation.

$P_{CO} = a_{FeO}\, a_c\, /a_{Fe} \exp(-\Delta G^0/RT)$

    a: activity (a_{FeO}, a_{Fe} : unit)

    ΔG^0: Gibbs standard free energy change in reduction reaction of FeO+C⇌Fe+CO

    R: gas constant

    T: sintering temperature

The author proved experimentally this hypothesis and proposed methods for the complete densification.

(2) Grain growth

(2.1) Numerical Calculation of WC Grain Growth in WC-Co Base Fine Grained Hardmetal[2]

The mean grain size of WC grains in commercial fine-grained WC-Co hardmetal are set above about 0.5 μm, although the more finer WC powders are commercially available. This seems to be because the grain growth becomes considerable, when the more finer WC powder is used. The cause for such considerable grain growth was not clear. Then, the authors derived an equation for WC grain growth in two-grain size alloy model and in multi-grain size alloy

model, where the growth mechanism is Ostwald ripening and the rate-determining step of the growth is the precipitation process.

For example, the large grain size in two-grain size alloy model is expressed by the following differential equation.

$$d_{L,t+\Delta t} = d_{L,t} + 4(2\sigma\kappa C_0 V_m^2/\nu RT)(1/d_{s,0} - 1/d_{L,t})\Delta t$$

$d_{L,t}$: size of large WC grain at sintering time of t

σ: interfacial energy of WC/Co

κ: interfacial reaction rate constant at WC/Co

C_0: equilibrium solubility (molar concentration) of WC in Co liquid phase

V_m: molar volume of WC

ν: correction factor which depends on shape and contiguity of WC grains

$d_{s,0}$: size of small grain at sintering time of zero

Δt: increment of sintering time

The result of calculation by using the experimental value of the term of $2\sigma\kappa C_0 V_m^2/\nu RT$ which corresponds to the slope of d_m^2-t curve showed that abnormal or considerable grain growth substantially occurs when the starting WC powder size becomes below about 0.2 μm.

(2.2)Preparation of Fine Grained Metals and Alloys with One Phase[3]

By hot pressing of ultra-fine Fe, Co and Ni metal powders with particle size of 0.02 μm, fine grained metals and alloy with mean grain size of 2.0- 0.09 μm were prepared. Hall-Petch relation between hardness and the inverse of square root of grain size was observed also in these fine grain size range in the same way as in the coarse grain size range above 10μm. The Vickers hardness (Hv) of, e.g., Fe metal and Fe-50at%Co alloy were extremely high irrespective of the absence of dispersed particles: about 600 at 0.09 μm and 900 at 0.12 μm, respectively. These values suggest that the yield strength (~1/3 of Hv) of these metal or alloy would reach about 2 GPa and 3GPa, respectively.

(3)Alloying or Generation of Compound

(3.1) Proposal of "Solution/Reaction-Precipitation Mechanism" for Generation of TiC-core/(Ti,Mo)-rim Structure in TiC-Mo₂C-Ni Cermet[4]

The carbide grains in TiC-Mo₂C-Ni cermet which is prepared from the mixed powder of TiC, Mo₂C and Ni show TiC-core/(Ti,Mo)C-rim structure, although the equilibrium carbide phase is only (Ti,Mo)C. The previous papers reported that the structure is supposed to be generated by solid diffusion of Mo and C atoms into the periphery of TiC grain. The author, et al., clarified that the structure is generated by the following "solution/reaction-precipitation mechanism".

(i)Smaller TiC grains and Mo₂C grains dissolve into Ni liquid phase.

(ii)Ti, Mo and C solutes in Ni liquid phase diffuse toward larger TiC grains and reaction-precipitate on the larger TiC grains in the form of (Ti,Mo)C phase, resulting in the generation of rim.

(iii)The thickness of (Ti,Mo)C-rim increases by Ostwald ripening, without the shrinkage of TiC-core.

(iv)The thickness of (Ti,Mo)C-rim further increases by a small amount by the precipitation of the solute during the cooling stage of sintering cycle.

The XMA analysis on Mo concentration profile in TiC-core/(Ti,Mo)C-rim structure supports the hypothesis.

(3.2) Proposal of New Hypothesis "Exhaustion of Diffusion-Contributable Vacancies in Core/Rim Structure"[5]

$FeSi_2$ is expected as a high temperature thermoelectric material. This is generated by a peritectoid reaction of $FeSi+Fe_2Si_5 \rightleftharpoons FeSi_2$, etc., in Fe-66.7at%Si alloy according to Fe-Si phase diagram. The reaction, however, hardly progresses even by long-time heating at high temperature, resulting in the generation of $FeSi$-core/$FeSi_2$-rim structure embedded in matrix of Fe_2Si_5 or $FeSi_2+Si$ which were generated by the decomposition of Fe_2Si_5. This phenomenon has traditionally been explained by the increasing of the rim thickness, i.e., the diffusion distance, accompanying the progress of the peritectoid reaction. In contrast with this, the author, et al., proposed the following new hypothesis "Exhaustion of Diffusion-Contributable Atomic-Vacancies in Core/Rim Structure".

(i) For the progressing of the peritectoid reactions, Si atoms in the matrix of Fe_2Si_5 or $FeSi_2+Si$ (Si-source) need to diffuse to the closed interface of $FeSi$-core/$FeSi_2$-rim (reaction site) via $FeSi_2$-rim, and at the same time the atomic-vacancies in $FeSi$-core and $FeSi_2$-rim should diffuse in counter-wise direction.

(ii) Such mutual counter-wise diffusions strongly suppress atomic-vacancies in the matrix to diffuse into $FeSi$-core and thus causes "the exhaustion of diffusion-contributable atomic-vacancies in $FeSi$-core and $FeSi_2$-rim structure", which causes the extremely slow rate of the peritectoid reaction.

This hypothesis could be verified by the fact that the reaction completely finishes near the compact surface where atomic vacancies are abundantly supplied.

This hypothesis can be applied to core/rim structure where the rim is a stoichiometric compound and the diffusion from core to rim and matrix is thermodynamically inhibited like in $FeSi$-core/$FeSi_2$-rim structure, and not to the structure where rim is not a stoichiometric compound and the mutual diffusion between core and rim is thermodynamically allowed like in TiC-core/(Ti,Mo)C-rim structure in TiC-Mo_2C-Ni cermet[6].

(4) Generation of Peculiar Surface Layer
(4.1) Generation of (W,Ti)(C,N)-Free Layer near Compact Surface of WC-(W,Ti)(C,N)-Co Alloy[7]

WC-(W,Ti)(C,N)-Co vacuum-sintered alloy which consists of WC+(W,Ti)(C,N)+Co three phases and usually contains also TaC, etc., is commercially used as the substrate alloy for CVD coated tools, because it has (W,Ti)(C,N)-free thin (about 10 μm) layer, i.e., WC+Co thin layer, near the compact surface and the layer has high resistance for the propagation of cracks in CVD-coated layer toward the substrate alloy. The author et al., proposed the following mechanism.

(i) Denitriding occurs from the compact surface.

(ii) Then, the N content or N+C content in Ni liquid phase near the compact surface decreases, which causes the increase of the equilibrium solubility of (W,Ti)(C,N) phase, i.e., contents of Ti and Mo, in Ni liquid phase near the compact surface.

(iii) Then, Ti, W and C solutes in Ni liquid phase diffuse from near the compact surface to the compact inside and precipitate on (W,Ti)(C,N) grains in the compact inside.

(iv) The processes from the above (i), (ii) and (iii) repeatedly continues, and thus (W,Ti)(C,N) grains disappears

near the compact surface, together with the growth of (W,Ti)(C,N) grains in the compact inside. The rate-determining step of the generation is not the denitriding process, but W and Ti diffusions toward the compact inside.

This mechanism clearly explain the experimental results on the influences of factors such as the contents of N, C and (W,Ti)(C,N) and the sintering atmosphere on the thickness of (W,Ti)(C,N)-free layer.

(4.2) Generation of Open Pores on Sintered Surface of Ti(C,N) Base Cermet[8]

Open pores, i.e., pores connecting to the compact surface, whose diameter are in the range of 10-100 μm, tend to be generated in Ti(C,N) base cermet. It was found that the generation occurs, when the atmosphere in the temperature-keeping stage during sintering is vacuum (7 Pa), irrespective of the kind of atmospheres (vacuum and nitrogen of 0.13 kPa) in the temperature-raising and cooling stage, and vice versa. The generation becomes more frequent at higher N/(C+N) atomic ratio of Ti(C,N) powder and/or at higher C content of cermet as far as the alloy is without free carbon phase and (Ti,Mo)$_3$Ni compound, i.e., θ-phase. The origin was clarified to be dents or cracks connecting the green compact surface.

The mechanism was supposed as follows.

(i) The growth of open pores is caused by denitriding from the compact surface to the sintering atmosphere. The denitriding occurs more rapidly from the compact surface having larger ratio of surface-area/volume.

(ii) Then, nitrogen concentration gradient occurs among the edge, side and bottom of dents or cracks and the general compact surface.

(iii) Such N concentration gradient causes the transports of Ti and Mo atoms mainly from the side and bottom of the dent or cracks to the edge. Such transports of Ti and Mo atom results in the deepening of the bottom and side and the protruding of the edge , which leads to the generation and growth of open pores.

The methods for inhibiting the generation of open pores were also proposed.

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