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STRUCTURE AND HARDNESS OF SINTERED Mo-Ni ALLOYS

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The Mo-Ni system is usually considered as a model system for studying the activated sintering process of a bcc refractory metal containing a ductile and less refractory fcc phase that acts as an activating imparting ductility [1]. The activated sintering process of the W-Ni and Mo-Ni systems containing small amounts of nickel (up to 0.7%*) was reviewed in detail by Uskokovich et al. [2]. Although there have been several approaches for describing the sintering mechanism of these alloys, it is more or less reliably established that intense volume diffusion of molybdenum (or tungsten) in nickel along with rapid diffusion of nickel along the surface and the grain boundaries of the parent metal takes place. Grain boundary segregation of nickel in molybdenum was recently observed using x-ray spectral analysis [3]. Lanam et al. [4] carried out a detailed study of the kinetics and the mechanism of sintering of the Mo-Ni alloys containing >70% nickel. To the best of our knowledge, there are no published data on the properties of the sintered alloys containing a low molecular fraction of nickel except for the data generated on the sintered alloys for establishing the phase (equilibrium) diagrams based on prolonged (up to several tens of days) high temperature annealing [5].

This paper deals with a study of certain properties of the sintered Mo-Ni alloys within a narrow range of concentrations.

Specimens of Mo-Ni powder mixtures containing 1, 5, 10, and 20% Ni were used. The original size of the molybdenum and nickel particles in the powder was 2-4 and 8 μm, respectively. Sintering was carried out in purified hydrogen atmosphere at a temperature of 1000-1300°C for a period of 1 h. In order to obtain a standard (reference) alloy of stoichiometric composition MoNi, we prepared a Mo-38% Ni† specimen and sintered it at 1200°C for a period of 2 h. The porosity was determined using the volumetric method.

X-ray analysis was carried out on a DRON-2,0 diffractometer using filtered CuKα-radiation. An accurate study of the MoNi alloy was carried out on a 'Philips PW1051' diffractometer using CuKα-radiation and a graphite monochromator. A 'Superprobe-733' microanalyzer was used for studying the fracture surface and the distribution of nickel in molybdenum. In order to obtain the fracture surface, a notched (filed) specimen was broken up under impact using a chisel. Vickers (sharpened diamond) indentation hardness was measured at a load of 1.15 N.

Table 1 shows the variation of porosity during the sintering process of the alloys. A rapid reduction of porosity was observed after sintering at 1200 and 1300°C; the reduction of porosity was found to be negligible at lower temperatures. Probably, interparticle contact formation is the main process occurring at these temperatures. Increasing the nickel content up to 20% significantly slows down elimination of porosity at a temperature up to 1200°C; at 1300°C, the nickel content has virtually no effect on the porosity.

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*Here and elsewhere, weight content of the elements is given.
†This alloy corresponds to the equiatomic composition MoNi.

TABLE 1. Effect of the Sintering Temperature on the
Porosity of Molybdenum—Nickel Alloys Sintered for 1 h

Condition of the specimen	Nickel content, %			
	1	5	10	20
Original	39,2	42,1	42,8	44,1
Sintered at a temperature, °C				
1000	38,0	37,6	40,4	43,1
1100	30,8	32,4	37,4	42,6
1200	16,5	13,2	16,3	23,7
1300	8.93	9,04	9,22	8,33

A similar relationship was previously observed in the sintered W—Ni alloys [2]; in this case, their retarded densification was attributed to the inhibition caused by the excess nickel phase and the weakening (disappearance) of the inhibiting effect with increasing temperature was attributed to accelerated diffusion and the formation of a solid solution. Evidently, the inhibiting action of the second phase significantly restricts the grain growth of the alloy having a high nickel content at elevated sintering temperatures. According to the phase diagram [6], the alloys of the investigated concentrations (1-20% Ni) must contain δ-phase, i.e., an intermetallic compound having a composition approximately corresponding to MoNi (precisely, Mo—37% Ni [5]). This intermetallic compound is hard and brittle [7] and its distribution along the grain boundaries leads to intergranular fracture (observed during the fractographic studies at all the sintering temperatures).

Precise x-ray analysis of the standard Mo—Ni alloy showed that it consists of a single phase having an orthorhombic lattice with $a = 0.9108$, b = 0.9108, and c = 0.8852 nm (space group $P2_12_12_1$). These characteristics exactly coincide with the parameters of the δ-phase of Mo—Ni [6, 8]. However, the intensities of a few lines of the δ-phase obtained under the aforementioned sintering conditions significantly differ from those calculated according to the method of Shoemaker and Shoemaker [8]. Probably, the δ-phase obtained under such sintering conditions is not a completely equilibrium phase. The intensity ratio of its lines varies as a function of the sintering temperature (Fig. 1). We note that in all the specimens sintered at the minimum experimental temperature (1000°C), the lines of nickel (or the nickel-based solid solution) are absent. Thus, virtually, the entirre nickel content of the alloys exists in the form of δ-phase or dissolves in molybdenum. The amount of δ-phase (characterized by the ratio of the intensities of the strongest line (313, 133) of the δ-phase (Fig. 1; $2\theta = 43.8°$) and the (200) line of molybdenum) increases with increasing sintering temperature (Fig. 2). Most probably, this increase is due to the insufficient concentration of molybdenum in δ-phase at low sintering temperatures and the transfer of molybdenum in δ-phase at low sintering temperatures and the transfer of molybdenum into δ-phase with increasing temperature. Thus, the intensity ratio I_δ/I_{Mo} increases not only due to increased I_δ, but also due to decreased I_{Mo}. At the same time, volumes diffusion of nickel in molybdenum increases quite slowly as compard to that of molybdenum in nickel [2, 7]. Figure 3 shows the lattice parameters of the experimental sintered Mo—20% Ni alloy along with the lattice parameters of the equilibrium solid solution based on molybdenum [5]. The variation of the lattice parameter indicates that when the alloy is sintered at 1000-1200°C, slight dissolution (not exceeding 0.4%) of nickel occurs in molybdenum and that at 1300°C, the concentration of dissolved nickel exceeds the limiting solubility in the equilibrium state (1.3%). However, the decrease in the lattice parameter of molybdenum may be partially due to the high vacancy concentration [2]. In view of this fact, after sintering at 1300°C, the obtained concentration of nickel in molybdenum is close to the equilibrium value. The significant change in the lattice parameter observed after sintering at 1300°C is accompanied by a marked widening of the x-ray diffraction lines of molybdenum (Fig. 2). It indicates the existence of considerable nonuniformity of the distribution of nickel dissolved in molybdenum and an increase in the dislocation density. According to Uskokovich et al. [2], [2], during the process of intense sintering, the dislocation density in the volume of the particles can increase up to approximately $10^9—10^{11}$ cm^{-2}.

The presence of point defects (substitutional solute atoms and vacancies) leads to a significant reduction of the intensity of the diffraction lines of molybdenum. This is reflected by the abrupt increase in the magnitude of the I_δ/I_{Mo} ratio of the specimens sintered at 1300°C (Fig. 2). A marked widening of the lines of the δ-phase is observed after
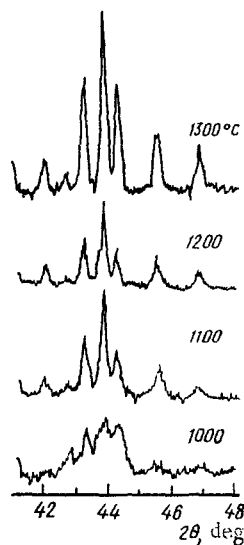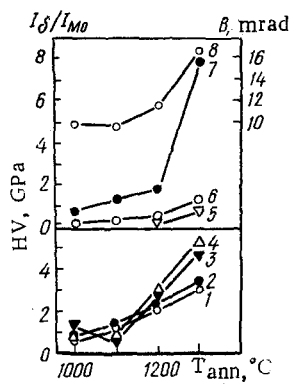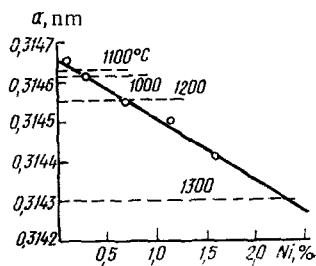
Fig. 1   Fig. 2   Fig. 3

Fig. 1. The portion of the x-ray diffraction pattern having the most intensive lines of the δ-phase in the Mo—20% Ni specimens sintered at different temperatures.

Fig. 2. Dependence of the microhardness (1-4), the intensity ratio of the (313, 133) diffraction lines of the δ-phase and the (200) line of molybdenum (5, 7), and the width of the $K_{\alpha1}$-component of the (321) line of molybdenum (8). Alloys: Mo—1% Ni (1), Mo—5% Ni (2, 5), Mo—10% Ni (3, 6), and Mo—20% Ni (4, 7, 8).

Fig. 3. Dependence of the lattice parameter of molybdenum in the Mo—20% Ni alloy on the sintering temperature (dashed lines) and on the nickel content in the equilibrium condition (solid line and the points).

TABLE 2. Intensity Ratio of the (313, 133) Line of the δ-Phase and the (200) Line of Molybdenum in the Mo—Ni Specimens Sintered at 1200°C for 1 h

Surface	Nickel content, %		
	5	10	20
External	0,118	0,51	1,31
Fracture	0,160	0,68	1,79

sintering at 1000°C, i.e., during the initial stages of the occurrence of diffusion of molybdenum into nickel (this indicates nonuniform distribution of molybdenum in δ-phase); at higher sintering temperatures, the lines of δ-phase become distinct and narrow (Fig. 1).

X-ray studies also confirm the predominant dispositioning of the δ-phase at the fracture surfaces (Table 2). X-ray spectral analysis shows highly nonuniform distribution of nickel along the fracture surface: under the characteristic nickel radiation, the intensity of certain regions is significantly higher that of the remaining regions (Fig. 4); furthermore, intergranular fracture mode is observed in all the regions (Fig. 4a) indicating the existence of nonequilibrium structural state. Microprobe study of the intensity variation of the characteristic radiation of nickel along the polished surface confirmed that segregation of nickel occurs not only at the grain surfaces, but also at the pore surfaces; however, the degree of segregation varies significantly at different regions. Uskokovich et al. [2] described the features of nickel distribution in the form of islets for a particular stage of sintering of the W—Ni alloy powders.
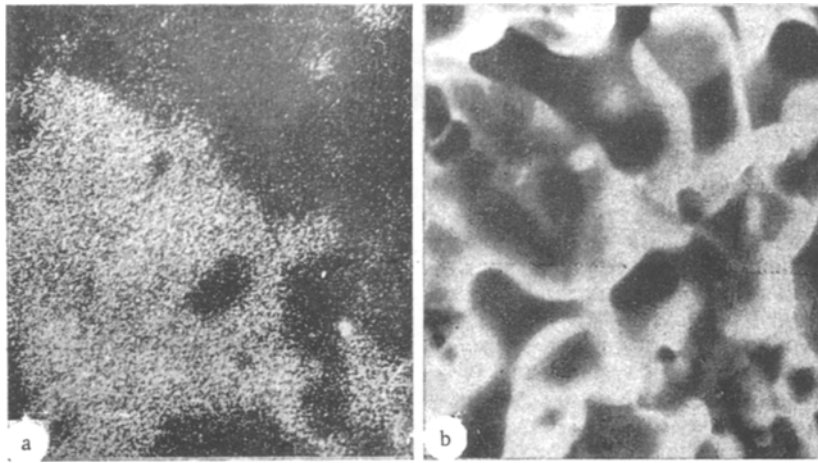
146

Fig. 4. Structure of the fractured region of the sin-
tered (1200°C) Mo—20% Ni alloy. ×6000. Secondary elec-
tron image (a); image under the characteristic Ni radia-
tion (b).

An analysis of the variation of hardness (Fig. 2) shows that at low sintering tempera-
tures (1000-1100°C), the hardness of all the alloys is significantly less than that of the
single crystals of molybdenum (approximately 1.2 GPa). As was shown earlier [1], such a
hardness reduction is due to the high porosity remaining at these sintering temperatures
(Table 1).

The observed increase in the hardness at higher sintering temperatures is mainly due to
the decreased porosity; however, the hardness of the alloys having a high nickel content
considerably exceeds the hardness of cast molybdenum and even the hardness of deformed
molybdenum containing a small amount of alloying elements [9]. The latter phenomenon may be
due to the precipitation of the intermetallic δ-phase (Fig. 2). The δ-phase obtained after
sintering the Mo—38% Ni alloy at 1300°C has a hardness of 8 GPa; this value is less than the
hardness of the equilibrium porefree δ-phase (12.6 GPa [7]). The hardness of sintered δ-
phase can decrease because of the presence of porosity (found to be 11%) and the aforemen-
tioned defects in the arrangement of atoms. Besides this, the hardness of the high-nickel
alloys sintered at elevated temperatures must increase due to strengthening of the molyb-
denum-based solid solution that leads to x-ray line broadening.

Thus, sintered Mo—(1-20) % Ni alloys are two-phase systems consisting of molybdenum and
δ-phase according to the phase diagram. The structure and the nonequilibrium state signif-
icantly depend on the chemical composition and the sintering regimes. The δ-phase is prefer-
entially distributed along the grain boundaries of molybdenum. An increase in the hardness
due to the presence of δ-phase takes place only when the porosity deceases up to 10-20%.

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COMPOSITE MATERIALS BASED ON HYDROGENATING

INTERMETALLIC COMPOUNDS

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The application of hydrogen accumulators in the automobile industry of foreign countries and the scientific and technological developments of the Soviet Union in this field are based on three intermetallic compounds that absorb hydrogen at room temperature, viz., TiFe, $LaNi_5$, and Ti_2Ni [1]. These intermetallic compounds were synthesized at the Institute for the Problems of Materials Science, Academy of Sciences of the Ukrainian SSR, using the powder metallurgy method and their sorption characteristics were studied in collaboration with the Institute of Gas, Academy of Sciences of the Ukrainian SSR [2-4].

The following problems are encountered when using the hydrogeneting intermetallic compounds. Introduction of hydrogen atoms into the lattice accompanied by the formation of a hydride leads to an increase in the specific volume of the lattice by approximately 25% because of which destruction (fragmentation) of the pieces (lumps) or the grains of the intermetallic compound and formation of dispersed powders take place. Such particulate bodies have very low thermal conductivity (because of high contact resistance) and their fine pores create a significant hydraulic resistance to the flow of hydrogen. This phenomenon leads to a significant deterioration of the important kinetic sorption—desorption characteristics since the rate of direct (exothermic) or reverse (endothermic) reactions is directly related to the rate of extraction and supply of heat and hydrogen. Besides this, fine powder particles are carried away by the gas flow which leads to the contamination of the system. Migration of the powder within the container can lead to localized densification (called 'caking') which can, in turn, lead to the destruction of the container under the action of tensile stresses.

These problems are solved by developing composite materials consisting of the particles of an intermetallic compound or its hydride that are bonded using a matrix made from a ductile material resisting fracture during hydrogenation. Thus, composite sorbing materials are developed in order to increase the thermal conductivity of the material and to ensure reliable retention (holding) of the dispersed hydride particles in the volume of the sorbent.

There have been numerous attempts [5-8] for obtaining composite hydrogenating materials. However, it has not been possible to obtain fracture resistant hydrogenating composites meeting the stringent specifications.

We produced composite materials based on the hydrogenating intermetallic compounds by compacting Ti_2Ni, TiFe and $LaNi_5$ powder mixtures with copper and nickel powders and subsequently sintering the compacts. We studied the hydrogenation characteristics of these materials at a high hydrogen pressure and the volumetric changes and the fracture mode during hydrogenation.

The curves presented in Fig. 1 characterize the dependence of sorption capacity on the hydrogenizing temperature at a hydrogen pressure of 0.1 MPa for the intermetallic compound

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