The formation of ternary compound Fe3Mo3C by ball milling

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Abstract

Ball milling of Mo in nitrogen and ammonia gases has been studied. After heating, the formation of an intriguing ternary compound, $Fe_3Mo_3C_{1-x}$, was observed as a result of Fe (and C) contamination from the milling apparatus. For a comparison, mechanical alloying of Fe−Mo−C powders with a stoichiometric composition of Fe_3Mo_3C was also performed and again an Fe−Mo−C alloy was obtained after milling. Thermal analysis shows a single transition peak for the formation of both the Fe_3Mo_3C phase in the latter case and also for $Fe_3Mo_3C_{1-x}$ formed as a result of contamination from the mill. The lattice parameter for the $Fe_3Mo_3C_{1-x}$ phase obtained by Mo-gas reaction is smaller than for the Fe_3Mo_3C phase obtained by mechanical alloying of stoichiometric Fe−Mo−C powders. It is suggested that, in the $Fe_3Mo_3C_{1-x}$ phase produced by milling of Mo in gases, a high concentration of C vacancies exists.

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Ball milling of Mo in nitrogen and ammonia gases has been studied. After heating, the formation of an intriguing ternary compound, $Fe_3Mo_3C_{1-x}$, was observed as a result of Fe (and C) contamination from the milling apparatus. For a comparison, mechanical alloying of Fe–Mo–C powders with a stoichiometric composition of Fe_3Mo_3C was also performed and again an Fe–Mo–C alloy was obtained after milling. Thermal analysis shows a single transition peak for the formation of both the Fe_3Mo_3C phase in the latter case and also for $Fe_3Mo_3C_{1-x}$ formed as a result of contamination from the mill. The lattice parameter for the $Fe_3Mo_3C_{1-x}$ phase obtained by Mo-gas reaction is smaller than for the Fe_3Mo_3C phase obtained by mechanical alloying of stoichiometric Fe–Mo–C powders. It is suggested that, in the $Fe_3Mo_3C_{1-x}$ phase produced by milling of Mo in gases, a high concentration of C vacancies exists. © *1995 American Institute of Physics.*

I. INTRODUCTION

Mechanical ball milling was first used in the late 1960s and early 1970s by Benjamin, Volin, and Bomford[1-3] for the development of dispersion-strengthened Ni and Al base superalloys. Many ball milling studies have been performed over the last 10 years, in particular, to produce a wide range of metastable (often disordered) phases. First, atomic disorder of intermetallic compounds was observed in the early stage of ball milling.[4,5] Second, amorphous alloys can be obtained by ball milling either elemental powders (mechanical alloying)[6,7] or intermetallic compounds (mechanical grinding).[8,9] In the mechanical alloying (MA) process, the driving force was considered to be the gain of free energy by alloying the elements, while nucleation of crystalline intermetallic compounds with an even lower free energy was kinetically suppressed. In the mechanical grinding (MG) process, atomic disorder was shown to be the major source of energy storage.[4,5] In some systems phase formation of solid solutions which exist in the phase diagram only at high temperature have also been found after room-temperature mechanical milling.[10,11] Finally, a mechanically induced phase transformation from a low-temperature crystalline phase to a complex high-temperature phase has been observed.[12,13]

Recently, many commercially interesting hard materials such as metallic and metalloid nitrides and carbides have been synthesized by the ball milling method.[14-16] The initial purpose of the present research was to prepare molybdenum nitride by solid-gas reaction during ball milling. Pure nitrogen and ammonia gases were used for the nitrogen sources. However, during the experiment, iron (and carbon) contamination from the milling environment was found to give rise to an intriguing ternary compound Fe_3Mo_3C in the end milling product. This ternary compound is a interesting material, especially when it exists together with Mo, thus forming a composite material. The results of the ball milling of Mo in nitrogen and ammonia gases are presented in this article. For a comparison, mechanical alloying of Fe–Mo–C powders with a stoichiometric composition of Fe_3Mo_3C was also performed.

II. EXPERIMENTAL PROCEDURE

Ball milling experiments were performed using a home-built planar-type milling device.[17] The device consists of a few hardened steel balls confined in a horizontal stainless-steel cylinder cell with 13 cm inner diameter. In the present experiments, four balls with a diameter of 2.5 cm were used. An external magnetic field was used to control the ball movement. For the solid–gas reaction, 5 g of pure molybdenum powder with a purity of 99.95% and particle size about 150 μm was charged in the stainless-steel cell. About 300 kPa of purified nitrogen or ammonia gas was sealed in the cell. The milling time was about 200 h. For mechanical alloying of Fe–Mo–C powders, 5 g of pure molybdenum, iron (purity better than 99% and particle size about 75 μm), and graphite (purity better than 99.9% and particle size about 50 μm) powders with a stoichiometric composition of Fe_3Mo_3C were used in the same device and milled for 194 h. The system was prepumped and then sealed.

X-ray-diffraction patterns were taken at room temperature by means of a Philips vertical powder diffractometer with Co $K\alpha$ radiation. Thermal analysis was performed in a Shimadzu DTA-50 thermal analyzer. Chemical analysis for C was performed in the Automatic Carlo Erba 1106 analyzer. The sample is combusted, and the gases, after scrubbing and reducing, are separated on a gas chromatograph column and measured at the detector.

Energy-dispersive x-ray analysis for Fe and Mo determination was carried out on a JEOL JSM 6400 scanning electron microscope (SEM) and microscopic structure of the samples was observed in a Cambridge Instruments S360 SEM fitted with a high-brightness lanthanum hexaboride (LaB_6) electron source. Mössbauer spectroscopy at room temperature, using a Rh^{57} Co source, was used to examine the annealed samples. Transmission electron microscopy (TEM) was also performed using a JEOL 2000 EX instrument.
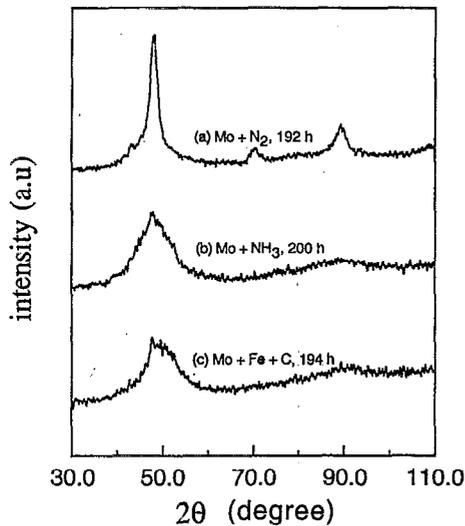
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FIG. 1. X-ray-diffraction patterns for (a) Mo milled in N_2 for 192 h, (b) Mo milled in NH_3 for 200 h, and (c) Mo, Fe, and C powders milled in vacuum for 194 h.

FIG. 3. X-ray-diffraction patterns for (a) Mo milled in N_2 for 192 h, (b) Mo milled in NH_3 for 200 h, and (c) Mo, Fe, and C powders milled in vacuum for 194 h and subsequently heated in DTA up to 1000 °C.

III. RESULTS

Three experiments have been performed in the present studies:

(1) Mo powder milled in nitrogen gas for 192 h;
(2) Mo powder milled in ammonia gas for 200 h;
(3) Mo, Fe, and C powders mechanical alloyed in vacuum for 194 h.

Figure 1 shows the x-ray-diffraction patterns of the materials prepared in the above three experiments. For Mo milled in N_2, the x-ray-diffraction patterns still show Mo crystalline peaks. The position of the peaks, however, shifts to high angle, suggesting that there is an absorption of N in Mo. For Mo milled in NH_3, amorphouslike diffraction peaks can be seen. The mechanical alloying of Mo, Fe, and C gives similar amorphouslike diffraction patterns. However, a preliminary TEM observation indicates crystalline diffractions
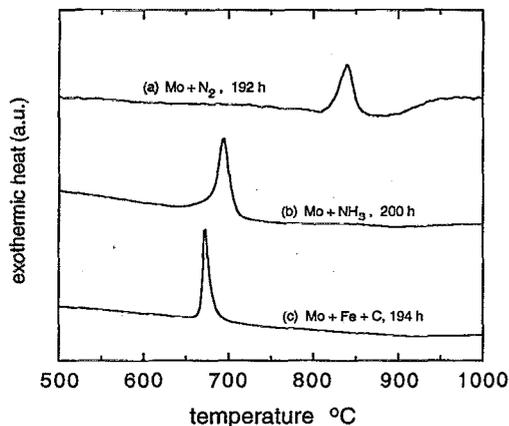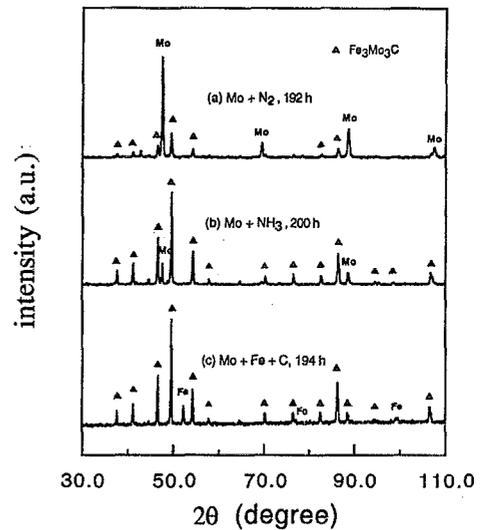
for both of these milled samples. This suggests that the elements have been mixed during milling to form very small crystals of a composite material, which results in amorphouslike diffractions in the x-ray patterns.

Results of the heating of the above three as-milled samples in DTA are given in Fig. 2 for a heating rate of 20 °C/min. For all three experiments, the heating of milled samples gives a single exothermic peak, which can be identified as the formation of a ternary compound Fe_3Mo_3C by

FIG. 2. DTA scans for samples: (a) Mo milled in N_2 for 192 h; (b) Mo milled in NH_3 for 200 h; and (c) Mo, Fe, and C powders milled in vacuum for 194 h. The heating rate is 20 °C/min.
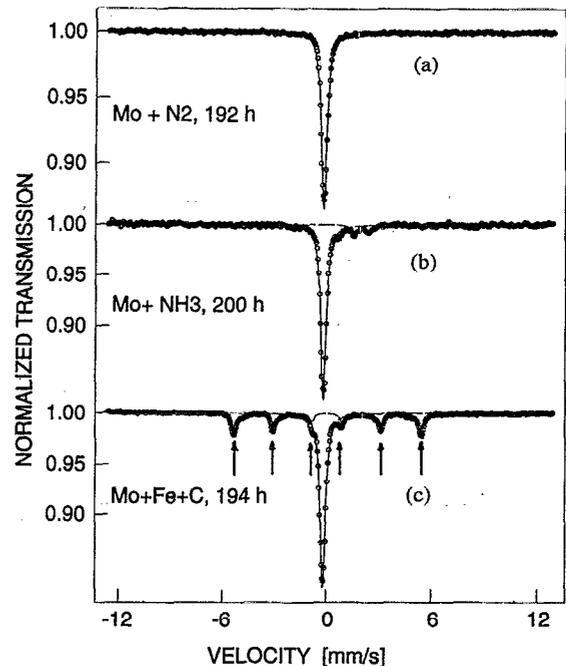

FIG. 4. Room temperature Mössbauer spectra for the three as-milled samples after heating to 1000 °C in DTA: (a) Mo milled in N_2 for 192 h; (b) Mo milled in NH_3 for 200 h; and (c) Mo, Fe, and C powders milled in vacuum for 194 h. The six-line spectrum shown by arrows is α-Fe.
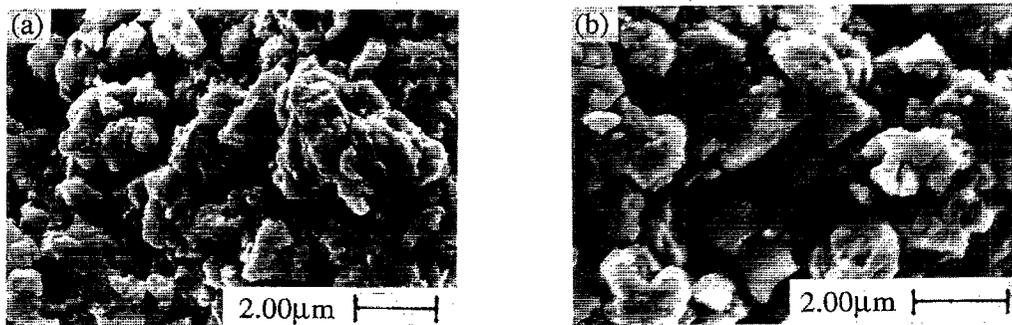
FIG. 5. SEM observations for powders of Mo milled in N_2 for 192 h: (a) as milled; (b) heated in DTA to 1000 °C.

examining the materials before the transition peak and after the transition peak by x rays; however, the peak temperature and heat of the phase formation are different, depending on the method of preparation. The peak temperatures are 840 °C for Mo milled in N_2, 695 °C for Mo milled in NH_3, and 675 °C for mechanical alloying of Mo, Fe, and C powders. The phase formation heats are 29 J/g for Mo milled in N_2, 49 J/g for Mo milled in NH_3, and 67 J/g for mechanical alloying of Mo, Fe, and C powders.

X-ray-diffraction patterns have been taken for each of the milled samples after heating in DTA up to 1000 °C. The results are shown in Fig. 3. From Fig. 3 it can be seen that for Mo milled in N_2, the Mo peaks become sharper, indicating the growth of Mo crystallites. Moreover, some new peaks appear, which can be identified as originating from the Fe_3Mo_3C phase. The intensities of Fe_3Mo_3C diffraction peaks are much smaller than Mo peaks, suggesting that there is only a minor amount of the Fe_3Mo_3C phase. For Mo milled in NH_3, the x-ray-diffraction patterns are similar to those of Mo milled in N_2. The only difference is that the relative intensity of the Fe_3Mo_3C diffraction peaks compared to Mo peaks is higher than in the case of Mo milled in N_2. For mechanical alloying of Mo, Fe, and C powders, x-ray diffraction shows the major Fe_3Mo_3C diffraction peaks with smaller Fe peaks.

The room-temperature Mössbauer spectra for the three as-milled samples after heating to 1000 °C in DTA are given in Fig. 4. From the bottom curve of Fig. 4, corresponding to the mechanical alloying of Mo, Fe, and C powders, the six-line spectrum, as shown (arrowed) in the figure, is characteristic of α-Fe. In addition, a dominant single line in the near-left-hand-side of center is also observed. From the x-ray-diffraction patterns in Fig. 3(c) it is believed that the Fe_3Mo_3C compound is the dominant phase in this material. Therefore, the single dominant line in the Mössbauer spectrum presented in Fig. 4(c) is believed to be the signal from the Fe_3Mo_3C phase. The middle curve in Fig. 4, for Mo milled in NH_3 and heated to 1000 °C shows no α-Fe spectrum. Besides the major line of the Fe_3Mo_3C phase, some other small peaks may originate from the mixture of Fe–Mo. For Mo milled in N_2 the Mössbauer spectrum (top curve in Fig. 4) shows clearly only the Fe_3Mo_3C phase, which suggests that in this sample all Fe impurity has formed the Fe_3Mo_3C phase. This result is in good agreement with the x-ray-diffraction data shown in Fig. 3(a), where only Fe_3Mo_3C and pure Mo diffractions have been observed.

Figures 5, 6, and 7 give SEM observations for all three ball-milled samples and also for the samples after heating to 1000 °C. From Figs. 5, 6, and 7 both particle size and morphology can be observed. For Mo milled in N_2, the particle size after milling is less than 1 μm [Fig. 5(a)], and grows to about 1–2 μm after heating to 1000 °C [Fig. 5(b)]. However, for the samples of Mo milled in NH_3 and mechanical alloying of Mo, Fe, and C powders,the particle size after milling is quite large, and is about 2–5 μm [Figs. 6(a) and 7(a)]. Moreover, after annealing the particle size becomes smaller in both latter samples [Figs. 6(b) and 7(b)].

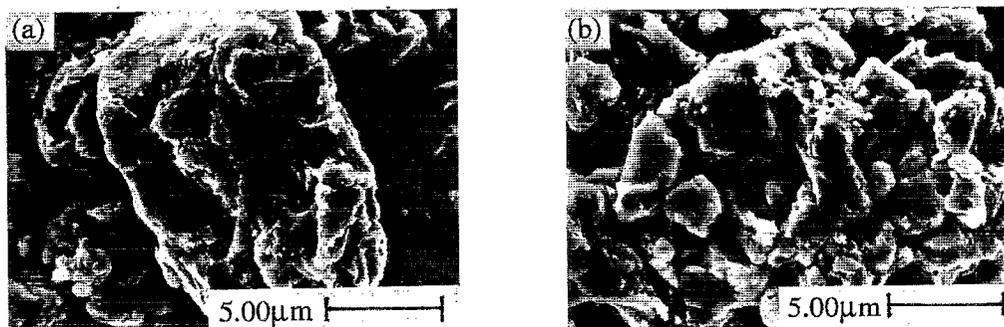Chemical analysis shows that 0.1 wt % C is present in

FIG. 6. SEM observations for powders of Mo milled in NH_3 for 200 h: (a) as milled; (b) heated in DTA to 1000 °C.
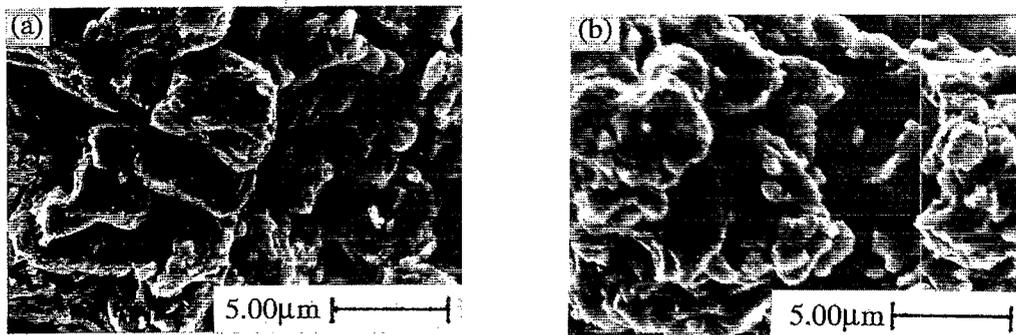
FIG. 7. SEM observations for samples of Mo, Fe, and C powders milled in vacuum for 194 h: (a) as-milled; (b) heated in DTA to 1000 °C.

the Mo milled in N_2 powder, 0.4 wt % C in the Mo milled in NH_3 powder, and 2.2 wt % C in the mechanical alloyed Mo–Fe–C powder. Furthermore, the elemental analysis for Fe and Mo carried out in the SEM shows 83 wt % Mo and 17 wt % Fe in the sample of Mo milled in N_2, 69 wt % Mo and 31 wt % Fe in Mo milled in NH_3, and 56 wt % Mo and 44 wt % Fe in mechanical alloyed Fe–Mo–C powder. In this case, C is neglected and the compositions of Fe+Mo are normalized to 100%.

The lattice parameters calculated from the x-ray diffraction patterns in Fig. 3 for the Fe_3Mo_3C phase are 11.077 Å for samples of Mo milled in both N_2 and NH_3 and 11.094 Å for the mechanical alloyed Fe–Mo–C sample.

IV. DISCUSSION

In Fig. 1 the bottom curve, mechanical alloying of Fe–Mo–C alloy, exhibits an amorphouslike diffraction pattern, where a large amount iron is present in the material (at least 35.8 wt % Fe). The middle curve—Mo milled in NH_3—also shows a similar amorphouslike diffraction pattern, indicating that a considerable amount of iron from the mill has contaminated the material. An Fe–Mo–C composite alloy is formed after milling for these two samples. In contrast, for Mo milled in N_2 (top curve in Fig. 1), x-ray-diffraction patterns show only broadened Mo diffraction peaks. This probably means that the iron contamination in the case of milling Mo in N_2 is small. The x-ray-diffraction patterns of the as-milled powders after heating to 1000 °C (Fig. 3) are consistent with this conclusion, because the relative intensity of the Fe_3Mo_3C phase in Fig. 3(a) is smaller than in Fig. 3(b). Suppose in the annealed Fe–Mo–C alloy, all the carbon has formed the Fe_3Mo_3C phase, then 2.2 wt % C from the chemical analysis gives a concentration of the Fe_3Mo_3C phase of 85 wt %. In the bottom curve of Fig. 3, pure α-Fe diffraction peaks have also been observed. This extra Fe content in the material may again come from contamination during milling. Using a similar calculation method, 0.4 wt % C gives an Fe_3Mo_3C content of 15 wt % for the material of Mo milled in NH_3, and 0.1 wt % C gives an Fe_3Mo_3C content of 4 wt % for the powder of Mo milled in N_2.

The above calculated amounts of the Fe_3Mo_3C phase seem to be too low in terms of the amounts expected from the upper two curves in Fig. 3, where the intensity of Fe_3Mo_3C diffraction peaks is not so small; However, because

the apparent relative intensity of x-ray-diffraction peaks is not a reliable measure of the relative amount of the phase present, the above estimates may still be valid. On the other hand, if all the Fe and C in the Fe_3Mo_3C phase comes from the milling apparatus, according to the formula of Fe_3C, the C content in the steel should be 6.8 wt %, which is much more than the actual value of 1 wt %. This suggests that the Fe content in the milled powders is considerably in excess of that necessary to form the Fe_3Mo_3C phase.

From the elemental analysis for Fe and Mo performed in the SEM, the amount of Fe_3Mo_3C phase can also be estimated. The results are: 49% of the Fe_3Mo_3C phase in the sample of Mo milled in N_2, 87% of the Fe_3Mo_3C phase in the sample of Mo milled in NH_3, and 91% of the Fe_3Mo_3C phase in the sample of mechanical alloyed Fe–Mo–C alloy.

The amounts of the Fe_3Mo_3C phase calculated from the measured C content and from measured Fe and Mo contents are very different. An explanation for the above discrepancy may be that, in the Fe_3Mo_3C phase formed by contamination of Fe and C from the milling apparatus, the C content is less than the stoichiometric composition, i.e., $Fe_3Mo_3C_{1-x}$; however, the $Fe_3Mo_3C_{1-x}$ phase is in the same cubic structure as stoichiometric Fe_3Mo_3C. It may be that a high concentration of C vacancies exists in the milled materials, where the Fe_3Mo_3C phase was formed by Fe and C from contamination. The lattice parameters calculated from the x-ray diffractions in Fig. 3 for $Fe_3Mo_3C_{1-x}$ phase produced by different methods give support for the above speculation. In fact, the lattice parameter for both the $Fe_3Mo_3C_{1-x}$ phase produced by Mo milled in N_2 and that produced in NH_3 is smaller than that for the Fe_3Mo_3C phase obtained by mechanical alloying of Fe–Mo–C powder, consistent with the notion of C vacancies. In addition, the amount of Fe_3Mo_3C phase estimated from the Fe and Mo analysis, and the consequential C content, is also consistent with this picture. In principle, there should be 2.4 wt % C present in mechanical alloyed Fe–Mo–C powder, which is very close to the actual value of 2.2 wt % obtained by chemical analysis. Thus, the Fe_3Mo_3C compound obtained by mechanical alloying of stoichiometric Fe–Mo–C powders and heated in the DTA up to 1000 °C contains few C vacancies. However, for Mo powder milled in N_2 and in NH_3, the measured C contents are very small, much less than that required for the stoichiometric Fe_3Mo_3C. Assuming C vacancies, we obtain compositions of

$Fe_3Mo_3C_{1-0.9}$ and $Fe_3Mo_3C_{1-0.8}$ for samples of Mo milled in N_2 and NH_3, respectively.

In Fig. 2, the single exothermic peak for all three samples is indicative of Fe_3Mo_3C phase formation, as shown by x-ray diffraction. Therefore, the differences in phase transformation temperatures and heats of formation shown in Fig. 2 can be related either to the amount of Fe_3Mo_3C phase or to different compositions and/or grain sizes present in the as-milled Fe–Mo–C composite alloy. The data obtained in this study on composition, structure, and thermal behavior indicate that the phase transformation on annealing is complex and it is difficult to separate the various contributions from each other.

The SEM results and also the x-ray data indicate the growth of Mo particle size after heating of the powder produced by milling Mo in N_2. Figures 6 and 7, however, suggest a decrease of the particle size after heating the samples of Mo milled in NH_3 and mechanical alloyed Fe–Mo–C powders. This is probably a result of the different phases present in the materials before and after heating. For both Mo milled in NH_3 and mechanical alloyed Fe–Mo–C powders, an Fe–Mo–C composite alloy is present after milling, and this transforms to the Fe_3Mo_3C phase after heating. Apparently the particle size for the Fe_3Mo_3C phase is very fine.

V. CONCLUSIONS

A Fe–Mo–C composite alloy is obtained by mechanical alloying of Fe, Mo, and C elemental powders. Subsequent heating in DTA to 1000 °C shows the formation of the Fe_3Mo_3C ternary compound. About 9 wt % Fe is also observed and this excess Fe originates from the milling apparatus. The lattice parameter for such Fe_3Mo_3C phase is 11.094 Å.

For mechanical milling of Mo in N_2 and in NH_3 gases, Fe (and C) contamination from the milling device is observed. 17 wt % Fe is found in the powder of Mo milled in N_2 and 31 wt % Fe is found in the powder of Mo milled in NH_3. After heating in the DTA apparatus up to 1000 °C, the formation of the compound $Fe_3Mo_3C_{1-x}$ is also observed in both samples. However, the C content obtained by chemical analysis is very small and we propose a high concentration of C vacancies in such samples. Moreover, the lattice param-

eter for $Fe_3Mo_3C_{1-x}$ phase in both samples is 11.077 Å. The smaller lattice parameter for the $Fe_3Mo_3C_{1-x}$ phase in samples of Mo milled in gases is consistent with the presence of C vacancies.

Finally, the present work illustrates the strong driving force for the formation of an $Fe_3Mo_3C_{1-x}$ ternary compound in competition with competing nitriding reaction. A further interesting aspect of the present work is the different, apparently stable composition (carbon content) of the end product. Mechanical testing of these different phases would be illuminating. Further work will concentrate on the study of the mechanical properties of such intriguing materials.

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