Composition Dependence of Microstructure of Mechanically Alloyed Powders and Their Compacts of High Nitrogen Cr-Mn Steels[†]

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Mechanical alloying (MA) of elemental powder mixtures, with an Fe-9.85 mass%N alloy powder as the nitrogen source, of the composition of Cr-Mn type stainless steels was carried out in an Ar atmosphere using a conventional planetary ball mill. In the MA processing of $\text{Fe}_{79-x-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_x$ (mass%) ($x=0.45$ and 0.9 ; $y=5-18$) material, the MA samples with $x=0.9$ is austenitized down to near $y=8$, whereas the MA samples with $x=0.45$ begin to austenitize near $y=11$. $\text{Fe}_{71.1-z}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_z\text{N}_{0.9}$ MA samples with Mo contents (z) in excess of 3% make the austenite phase, formed in the MA powder materials, less stable. Using a hot-rolling technique tried in the current study, the compact sample of $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ MA powder material was fully densified, retaining the nanostructure. Addition of AlN to the MA material of $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ made it possible to suppress the grain growth in the compact sample, to a considerable extent, during hot-compaction using the rolling process.

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I. Introduction

Nitrogen alloying is an effective way to improve mechanical and chemical properties of stainless steels, especially austenitic ones. Because of such positive effects of nitrogen, much attention has increasingly been paid to high nitrogen containing austenitic stainless steels as a new class of engineering materials. In addition, since nickel free high nitrogen austenitic steels, like high nitrogen Cr-Mn austenitic steels, do not emit Ni ions causing nickel allergy in contact with human body, they are also noticed as one of promising biomaterials nowadays⁽¹⁾. High nitrogen steels are commonly produced using high nitrogen pressure processing techniques such as high-pressure melting-solidification and high-pressure, solid-state diffusion at high temperature.

Recently, it is noticed that mechanical alloying (MA) of powder materials of iron-based alloys in an atmospheric nitrogen gas and MA of powder mixtures of metal nitrides and iron-based alloys are very effective nitrogenization techniques⁽²⁾⁻⁽⁴⁾. One advantage offered by nitrogenization using the MA process is formation of nanostructured powder products, because it leads to bulk materials, which generate high performances resulting from the nanostructured character, by appropriate consolidation processes such as sintering.

In the current work, we tried to manufacture high nitrogen Cr-Mn type austenitic steel powders by MA of powder mixtures of elemental metals and an iron nitride powder and to consolidate the MA-processed powders for a relatively short period using a hot-rolling process.

The aim of this work is to investigate effect of the composition of the present materials on microstructures of the MA-processed powders and their hot-consolidated compacts such as austenitized structures and nanostructures originally developed during the MA processing.

II. Experimental Procedure

The alloy powder materials of the composition $\text{Fe}_{82-x-y-z}\text{Cr}_{18}\text{Mn}_y\text{Mo}_z\text{N}_x$ (mass%) ($x=0.45$ and 0.90 ; $y=5-18$; $z=0-5$) were prepared by mechanical alloying (MA) of powder mixtures of pure elemental powders (particle size: 63–149 μm) and an Fe-9.58 mass%N alloy powder (mean particle size; 147 μm) as the nitrogen source using a planetary ball mill which is the same as that employed previously⁽⁵⁾. The MA processing time was 720 ks. In order to examine compositional dependence of austenitizing of the MA samples thus obtained, characterization of the samples was performed by X-ray diffraction (XRD) (CoK_α radiation, $\lambda=0.17902$ nm) and/or magnetic measurements using a vibrating sample magnetometer (VSM).

In hot-compaction experiments, austenitic MA powder samples, whose austenitic phases are taken to be stable during the compaction, were used. Each of these MA powder samples weighting about 7 g was vacuum-charged under a hydraulic pressure into a 316 stainless steel pipe of 10 mm outside diameter and 0.5 mm wall thickness; the inner part of the pipe filled with powder of about 7 g resulted in its heights of ca. 20 mm. After solution annealing the MA powder samples thus charged in the pipe, they were hot-compacted at temperatures between 800–1200 K using a conventional laboratory two-high rolling mill with 70 mm-diameter rolls. The surface velocity of rolls was 0.16 m/s. The rolling operation was

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performed through two passes. The first pass yielded a reduction corresponding to 30% of the outside diameter of the MA powders charged pipe, resulting in formation of the plate-like product in shape. The second one yielded 80% reduction in thickness of the plate-like product. The thickness of the MA material layer consolidated in the final products thus rolled was approximately 1.5 mm or so.

Phases present in the MA materials before and after hot-compaction were mainly identified by the XRD analysis. The microstructures of the compact samples consolidated were also examined from metallographic observations of the cross-section using an in-lens type field emission scanning electron microscope (FE-SEM, Hitachi S-5000). Samples for FE-SEM examinations were prepared by Ar ion etching. In addition, from Bragg peaks in the XRD patterns, the grain size in materials before and after hot-compaction was calculated using Scherrer's formula⁽⁶⁾. The contents of nitrogen in MA materials before and after hot-compaction were determined by an inert gas carrier melting-thermal conductimetric method.

III. Results and Discussion

1. Mechanical alloying and austenitizing of Fe-Cr-Mn-Mo-N materials

Figure 1 shows the X-ray diffraction (XRD) patterns for MA powders of $\text{Fe}_{78.55-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_{0.45}$ ($x=0.45$) and $\text{Fe}_{78.1-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_{0.9}$ ($x=0.9$) with the indicated y values. In the figure, it is noticed that the MA samples with $x=0.9$ were austenitized down to near $y=8$ (Fig. 1(b)), whereas the MA samples with $x=0.45$ started to austenitize at $y=11$ (Fig. 1(a)). This suggests that the austenite stability with respect to strain-induced martensite formation is highly enhanced by N, even under an

Fig. 1. X-ray diffraction patterns (XRD) for (a) $\text{Fe}_{78.55-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_{0.45}$ and (b) $\text{Fe}_{78.1-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_{0.9}$ MA powders with the different values of y indicated. CoK_α radiation ($\lambda=0.17902$ nm). γ : austenite; α' : martensite (or ferrite).

extremely heavy deformation like the MA processing.

Figure 2 shows the XRD patterns for MA powders of $\text{Fe}_{71.1-z}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_z\text{N}_{0.9}$ ($x=0.9$; $y=10$) with different values of z . It is well known that molybdenum distinctly increases nitrogen solubility but primarily leads to a marked improvement in corrosion resistance properties in nitrogen bearing steels⁽⁷⁾. It is demonstrated, however, that high contents of Mo in excess of 3 mass% make the austenite phase in MA materials less stable.

The XRD results of Figs. 1 and 2, showing compositional dependence of austenitizing of MA materials, were also confirmed from magnetic measurements of them. Magnetization M_{max} of $\text{Fe}_{78.1-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_{0.9}$ MA samples at room temperature in the applied field of 1200 kA/m is presented as a function of Mn concentration y in Figure 3 where the magnetization M_{max} steeply decreases in the vicinity of $y=8$. The results shown in Figure 3 are substantially consistent with those of Fig. 1(b).

2. Hot-compaction of MA-processed powder samples

The MA samples, whose austenitizing is confirmed by XRD and VSM measurements, of (a) the

Fig. 2. XRD patterns for $\text{Fe}_{71.1-z}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_z\text{N}_{0.9}$ MA powders with the different values of z indicated.

Fig. 3. Magnetization M_{max} of $\text{Fe}_{78.1-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_{0.9}$ MA samples at room temperature in the applied field of 1200 kA/m as a function of the Mn concentration y .

Fig. 4. XRD patterns for $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ MA powders isothermally aged at 873 K (a), 973 K (b), 1073 K (c), and 1173 K (d) for the indicated different times t after vacuum-charging into a stainless steel pipe and solution annealing at 1273 K for 3.6 ks, followed by cooling in water. γ : austenite; α : ferrite.

$\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ material and (b) the $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ material containing 5 vol% AlN were employed in hot-compaction experiments. Addition of AlN to the MA sample of $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ was performed by mechanical processing for 1.8 ks using the ball mill utilized in the present work.

Prior to the hot-compaction experiments, we tried to tentatively determine a time-temperature-precipitation (TTP) diagram for the precipitation of Cr_2N , which is detrimental to the toughness and corrosion resistance properties of N-alloyed austenitic stainless steels⁽⁸⁾, regarding the MA samples of the material (a). After vacuum-charging into a stainless steel pipe and solution annealing of the MA samples of (a) at 1273 K for 3.6 ks, followed by water quenching, they were isothermally aged in the range 873 K to 1173 K for the times ranging from 0.03 to 172.8 ks. The XRD results of aged samples are exhibited in Fig. 4. In the present system, chromium nitride Cr_2N is observed to precipitate most rapidly at a temperature near 1073 K after nucleation of some ferrite phase in the matrix, unlike the case of high nitrogen Cr-Ni austenitic stainless steels where the first phase to precipitate has been reported to be chromium nitride⁽⁹⁾.

In Figure 5, an isothermal TTP diagram for Cr_2N precipitation of the solution annealed material (a) tentatively depicted using the XRD data of Fig. 4 is illustrated. On the basis of this diagram, hot-compaction of MA powders of the materials (a) and (b) was performed through two rolling passes (Fig. 6) at each temperature of 873, 973, and 1173 K where the austenite phase is considered to be comparatively stable. Densification in the compacts of both the materials increased with increasing compacting temperature, as expected, so that any microvoids were not observed in the compacts consolidated at 1173 K as illustrated in Fig. 7 showing FE-SEM micrographs of the cross-sections of the compact samples of (a) and (b) materials fabricated at 1173 K. In addition, it is noticed that the microstructure of the material (b)

Fig. 5. TTP diagram for Cr_2N precipitation in the solution annealed $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ MA samples.

Fig. 6. Schematic representation of hot-rolling process.

containing 5 vol% AlN is considerably fine as compared with that of the material (a) without the additive of AlN. Since the average grain size of these compacted samples is taken to be approximately 15–20 nm (Table 1), each microstructure in Fig. 7 seems to reveal the cross-section of an aggregate of individual particles, with a size range of ca. 300–500 nm, composed of such grains of several tens of nanometers. Furthermore, the results of chemical analysis of samples (a) used in the hot-compaction at 1173 K showed that nitrogen contained in the MA samples is retained in the hot-compacted samples as follows. As-MAed sample: 0.88 mass%N; compacted sample: 0.89 mass%N.

Fig. 7. FE-SEM micrographs of the cross-sections of compact samples of (a) $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ material and (b) $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ material containing 5 vol% AlN consolidated at 1173 K.

Table 1 Grain size of $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ samples before and after hot-compaction.

	As-MAed	Hot-rolled*	As-MAed	Hot-rolled*
Additive	—	—	5 vol%AlN	5 vol%AlN
Average size (nm)	8.6	20.0	8.6	15.2

* hot-rolled at 1173 K and water-quenched.

IV. Conclusions

This brief paper on manufacture and compaction of Cr-Mn type stainless steel powders leads to the following conclusions:

(1) In mechanical alloying (MA) of $\text{Fe}_{79-x-y}\text{Cr}_{18}\text{Mn}_y\text{Mo}_3\text{N}_x$ (mass%) ($x=0.45$ and 0.9 ; $y=5-18$) material from elemental powder mixtures, with iron nitride powders, using a planetary ball mill, the $x=0.9$ MA samples can be austenitized down to near $y=8$, while the $x=0.45$ MA samples start to austenitize near $y=11$.

(2) $\text{Fe}_{71.1-z}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_z\text{N}_{0.9}$ MA materials with Mo contents (z) of more than 3% make the austenite phase less stable.

(3) Using a hot-rolling technique tried in the present work, the compact sample of $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$ MA powder material is completely densified and its nanostructure is retained.

(4) Due to addition of AlN to the MA material of $\text{Fe}_{68.1}\text{Cr}_{18}\text{Mn}_{10}\text{Mo}_3\text{N}_{0.9}$, it is possible to suppress the grain growth in the compacted sample, to a considerable extent, during hot-compaction using the rolling technique.

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