CHIN.PHYS.LETT. Vol. 25, No. 7 (2008) 2607

Mn Nanowhiskers of a Novel Hexagonal Phase Grown from Hydrogen Activated Laves Phase Alloys *

WU Er-Dong(吴尔冬)**, GUO Xiu-Mei(郭秀梅)

Shenyang National Laboratory for Material Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016

(Received 29 January 2008)

With the aid of hydrogenation/dehydrogenation, nanorod whiskers of transition metal Mn can grow spontaneously from $Zr_{1-x}Ti_xMnCr$ Laves phase alloys at room temperature. The finding introduces a distinguishingly different element into metal whisker family, and provides a potential technique for fabrication of one-dimensional metal nanostructures. Moreover, it is found that the segregated Mn in whiskers forms a novel hexagonal structure, which partially fulfills the long predicted allotropic form and adds more complexity to the structures of Mn.

PACS: 68. 70. +w, 61. 46. Km, 61. 66. Bi

The Zr and Ti-based AB_2-type Laves phase alloys have been extensively investigated as promising hydrogen storage materials.[1−3] Among these alloys, the C14-type hexagonal $Zr_{1-x}Ti_xMnCr$ alloys exhibit high storage capacity, low hysteresis and good activation properties for hydrogenation.[4] Further, in the powder specimens of hydrogen activated $Zr_{1-x}Ti_xMnCr$ alloys, a new physical phenomenon, i.e. the spontaneous room-temperature growth of Mn nanowhiskers with a novel hexagonal structure, was observed. In this Letter, we report our findings in the observation.

TEM images [Figs. 1(a) and 1(b)] of the hydrogen activated specimens after exposed for more than 15 h show that some whiskers sprout from inside of the single crystals of the alloys. The shape of a typical whisker can be described as nanorod with a diameter of about 10–100 nm and several hundred nanometres long [Figs. 1(a)–1(c)]. However, nanowires of lengths up to about 3 μm are also observed [Fig. 1(d)]. A comparison among nanowhiskers observed in the alloys with different Ti content x shows that though the formation of the nanowhiskers can be observed in all specimens with different x from 0 to 0.5, the alloy with $x = 0.1$ shows the highest distribution density and largest size dimension of nanowhiskers. The selected area diffraction (SAD) study indicates that most of the nanowhiskers are single crystals, though multi-crystalline nanowhiskers are also observed. The analyses of the SAD patterns (see Fig. 2) of the nanowhiskers reveal that the crystals have a primitive hexagonal unit-cell with lattice parameters $a = 1.05(2)$ nm, $c = 0.31(1)$ nm. The EDS measurements confirm that the compositions of the bulk crystals are consistent with the nominal compositions of the samples, while reveal that the nanowhiskers are actually made of Mn element (see Fig. 3). The Mn segregation associated with a compositional gradient between the root of the nanowhisker and the bulk of the crystal is also observed. However, small fractions of the Laves phase component elements of Cr, Zr and Ti, or small amount of oxygen up to 20% are also detected in some of the nanowhiskers, indicating incomplete segregation or oxidation of Mn in these nanowhiskers. The SAD patterns indicate that the nanowhiskers grow along the c-axis of their hexagonal lattice, and approximately along the basal plane of the Laves phase lattice (see Fig. 4). The nanowhisker has not been observed either in the unactivated specimen or the specimen immediately exposed, suggesting that the sample activation and exposition both have played roles in the formation of the nanowhiskers. It is observed that the crystals of the Mn nanowhiskers are unstable under an electron beam, and would quickly

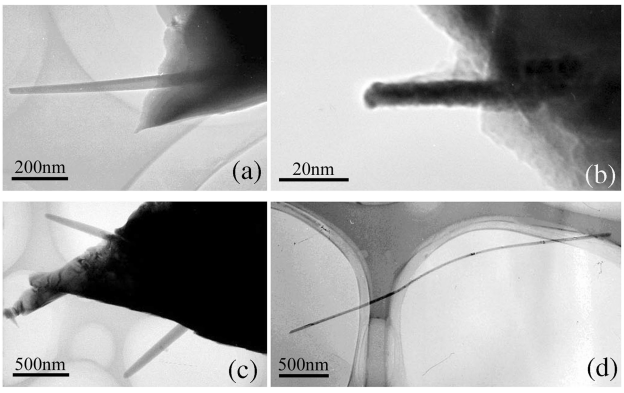

Fig. 1. Appearances of the nanowhiskers grown from the hydrogen activated $Zr_{1-x}Ti_xMnCr$ alloys from the TEM photographs: (a) a nanorod sprouts from inside of a single crystal; (b) a tiny nanorod from a crystal; (c) more than one nanorods grow on a crystal grain; (d) a nanowire in diameter of about 30 nm and in length of about 3 μm.

*Supported by the National Natural Science Foundation of China under Grant No 50371086.

** Email: ewu@imr.ac.cn

© 2008 Chinese Physical Society and IOP Publishing Ltd

transform into amorphousness during TEM examination. Hence, this hexagonal phase is likely to be a metastable phase. In the XRD pattern, peaks at positions consistent with the SAD study are not found, indicating that the yield of the nanowhiskers is lower than 1%.

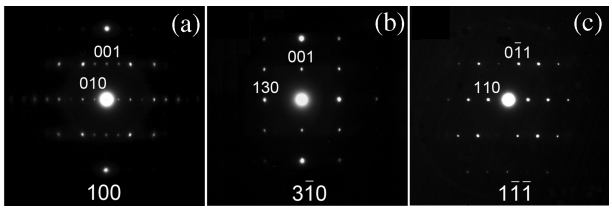

Fig. 2. SAD measurements of the Mn nanowhiskers: (a)–(c) the SAD patterns are indexed as a primitive hexagonal unit-cell with $a = 1.05(2)$ nm, $c = 0.31(1)$ nm. The zone axis of each pattern is shown at the bottom centre of the pattern.

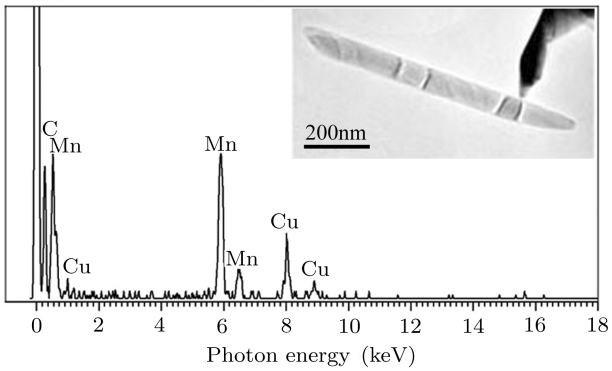

Fig. 3. EDS measurement of a typical nanowhisker. Only element Mn from the separated nanowhisker shown on the top right corner picture, and Cu and C from TEM system can be detected.

Previously, spontaneous room-temperature growth of whiskers was only observed for soft metal elements with low melting points in the element period table from late transition metal groups up to group VA, such as Sn and Zn.[5−10] As Mn is a hard ($H_v = 500$) earlier transition metal with higher melting point (1244°C),[11] and this type of metals such as Mo can only develop whiskers at elevated temperatures,[6] we have significantly reduced the whisker growing temperature by hydrogenation, and added a distinguishing element to the metals capable of spontaneously growing whiskers. Though soft metals can develop nanowhiskers,[8,9] most whiskers possess a size in micrometre scale, and form various irregular shapes,[5−10] whereas the morphology of the Mn whiskers is regular shaped nanorod. In comparison with most soft metals, where whiskers are found on the surface of individual grains or at the grain boundaries of the polycrystalline alloys,[5−10] the Mn nanowhiskers are segregated from inside of the crystal grains. Various mechanisms, all attributed to a compressive stress, have been proposed for the spontaneous growth of metal whiskers.[5−7] Such assumption seems to be consistent with our case, where Mn has a lowest melting point among the component alloying elements, and its harness is lower than that of the Laves phase (the hardness of $x = 0.1$ alloy is measured as $H_v = 970 \pm 50$). As hydrogenation is essential for the formation of Mn nanowhisker, it should be the primary cause of the phenomenon. Although hydrogen in the crystal lattice can provide compressive stress, we find that an incubation time after the samples exposition to air is a necessary prelude to evidence of Mn nanowhisker, which means that the hydrogenation alone can not provoke the growth of whiskers, and the exposition process appears to trigger a reaction for growth of the whiskers. A plausible interpretation attributes the frictional compressive force to extrude whiskers out to a volume expansion created by a reaction between oxygen and the sprouting metal.[7] Similarly, oxygen and hydrogen in the lattice of the alloy could react and create heat and volume expansion, providing energy and force required for the whisker growth. However, the oxidation theory is based on the segregated metal from grain boundaries,[7] whereas Mn is alloyed in the crystal lattice where oxygen is difficult to diffuse and has not been detected in the EDS measurements. Therefore, the detailed mechanism of the growth of Mn whisker is still unclear.

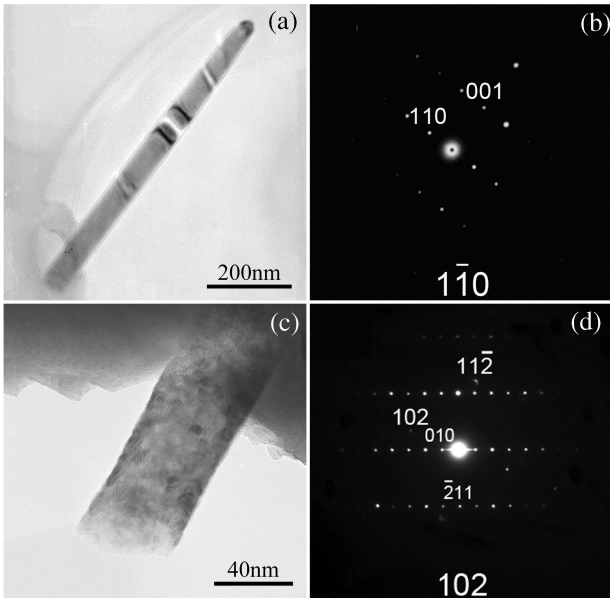

Fig. 4. Orientations of the nanowhiskers: (a) a Mn nanowhisker, and (b) its corresponding SAD pattern; (c) the TEM image of a nanowhisker and the adjacent crystal; (d) the corresponding SAD pattern showing the diffraction spots of hexagonal lattices of both the nanowhisker (small indices and corresponding zone axis at the centre bottom of the pattern) and the Laves phase (large indices).

In comparison with other metals, structures of ele-

mental Mn are relatively complex. The element forms four types of cubic allotropic phases at various temperatures at ambient pressure. As a VIIB element, Mn would be expected to form an *hcp* structure.[12] However, due to the disturbance of the magnetism of the 3*d* electrons of Mn, its room-temperature polymorph, like an intermetallic compound, has an exotic cubic unit-cell containing 58 atoms with various interatomic distances and coordination numbers.[12,13] The possibility of forming an *hcp* structured Mn has long been predicted, but never been realized.[14−16] The observation of this hexagonal phase has partially fulfilled the prediction, but added more complexity to the structures of Mn. In comparison with most intermetallic compounds, the lattice parameters of this hexagonal phase are quite unusual, as the *c*-axis of the unit-cell is significantly smaller than that of the *a*-axis, and approaching to the metallic size of Mn element (0.254 nm).[17] Based on the density of α-phase Mn,[13] the unit-cell of the hexagonal Mn would have 24 atoms (Pearson symbol hP24, density of about $7.4\,\mathrm{g/cm^3}$), leading to a new structure. On the other hand, if two atoms are added in the unit-cell, the $Cu_{10}Sb_3$[18] type superstructure modified from the *hcp* structure could be considered, where the Mn–Mn distances will approximately be in the range of 0.22 to 0.31 nm, comparable to the distances of between 0.226 to 0.293 nm in α-Mn.[13] The possibility to stabilize unusual phases of materials in nanocrystal form by finite size effect has generated great interest.[19] A novel β-Mn type of Co in the form of nanocrystalline thin films has been synthesized by solution-phase metal salt reduction.[20] On the other hand, the syntheses of Se and Te nanowires[21] and Co nanorods[22] have indicated that the hexagonal lattices are favourable for the crystallization of one-dimensional nanostructures. Therefore, the stabilization of the unusually low *c*-axis hexagonal structure may be attributed to the combined constraints of the one-dimensional nanoscale morphology of the whiskers and the disturbance of the magnetism of Mn.

In summary, Mn is an important magnetic element.[14−16] However, up to now, the synthesis of one-dimensional Mn nanorods or nanowires has not been reported. Our discovery has thus provided a potential technique for fabrication of novel structured metals, and opens up perspectives for the fundamental research on the hexagonal-structured Mn.

We thank Li Yu-Sheng, Zheng Shi-Jian and Yang Chun-Na for help in the TEM experiments.

References

[1] Sinha V K, Pourarian F and Wallace W E 1982 *J. Alloys Compd.* **87** 283
[2] Liu B H, Kim D K, Lee K Y and Lee J Y 1996 *J. Alloys Compd.* **240** 214
[3] Huang T Z, Wu Z, Yu X B, Chen J Z, Xia B J, Huang T S and Xu N X 2004 *Intermetallics* **12** 91
[4] Guo X M and Wu E 2008 *J. Alloys Compd.* **455** 191
[5] Galyon G T 2004 *A History of Tin Whisker Theory: 1946 to 2004.* 2004 *SMTA Int. Conf. Proc.* (Chicago, IL) **26-30** 696
[6] Arnold S M 1956 *Tech. Proc. 43rd Annual Conv. Am. Electropl. Soc.* p 26
[7] Barsoum M W, Hoffman E N, Doherty R D, Gupta S and Zavaliangos A 2004 *Phys. Rev. Lett.* **93** 206104
[8] Cheng Y T, Weiner A M, Wong C A, Balogh M P and Lukitsch M J 2002 *Appl. Phys. Lett.* **81** 3248
[9] Sun Z M and Barsoum M W 2005 *J. Mater. Res.* **20** 1087
[10] Barsoum M W and Farber L 1999 Science **284** 937
[11] Ross R B 1992 *Metallic Materials Specification Handbook* 4th edn (London: Chapman)
[12] Hobbs D, Hafner J and Spišák D 2003 *Phys. Rev.* B **68** 014407
[13] Oberteuffer J A and Ibers J A 1970 *Acta Cryst.* B **26** 1499
[14] Asada T and Terakura K 1993 *Phys. Rev.* B **47** 15992
[15] Hujihisa H and Takemura K 1995 *Phys. Rev.* B **52** 13257
[16] Zheng-Johansson J X, Eriksson O, Johansson B, Fast L and Ahuja R 1998 *Phys. Rev.* B **57** 10989
[17] Pauling L 1960 *The Nature of the Chemical Bond* (New York: Cornell University)
[18] Günzel E and Schubert K 1958 *Z. Metallkd.* **49** 124
[19] Tolbert S H, Herhold A B, Brus L E and Alivisatos A P 1996 *Phys. Rev. Lett.* **76** 4384
[20] Sun S and Murray C B 1999 *J. Appl. Phys.* **85** 4325
[21] Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, Yin Y, Kim F and Yan H 2003 *Adv. Mater.* **15** 353
[22] Puntes V F, Krishnan K M and Alivisatos A P 2001 *Science* **291** 2115