Crystallization study of amorphous $\text{Mn}_{1-x}\text{C}_x$ films prepared by RF magnetron sputtering

A. Aouni, E. Bauer-Grosse

► To cite this version:

A. Aouni, E. Bauer-Grosse. Crystallization study of amorphous $\text{Mn}_{1-x}\text{C}_x$ films prepared by RF magnetron sputtering. Journal de Physique IV Proceedings, 1993, 03 (C7), pp.C7-2189-C7-2192. 10.1051/jp4:19937349 . jpa-00251997

HAL Id: jpa-00251997

<https://hal.science/jpa-00251997>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Crystallization study of amorphous $\text{Mn}_{1-x}\text{C}_x$ films prepared by RF magnetron sputtering

A. AOUNI and E. BAUER-GROSSE

Laboratoire de Science et Génie des Surfaces, URA 1402 du CNRS, Ecole des Mines, Parc de Saurupt, 54042 Nancy cedex, France

Abstract.

For the first time, $\text{Mn}_{1-x}\text{C}_x$ amorphous films with $0.20 \leq x \leq 0.37$ were obtained by RF magnetron sputtering. Their thermal stability was studied by DSC and hot stage TEM. For $x \leq 0.34$, the crystallization of amorphous alloys leads to the formation of known triangular prismatic sheet (TPS) carbides such as Mn_3C and Mn_5C_2 , and in addition, to the formation of new metastable TPS carbides having either periodic structures which correspond to $\text{Mn}_{2n+1}\text{C}_n$ formula with $n = 3$ and $n = 4$ or one-dimensional aperiodic structures with the $\text{Mn}_{1-y}\text{C}_y$ formula. This structure type can lead to the TPS Mn_2C carbide which have been detected for $x = 0.34$. For $x \geq 0.34$ a new percarbide Mn_2C , for which C atoms are in octahedral interstices, is observed.

Introduction.

The aim of this work is to study the structure and defects of metastable carbides which appear during the crystallization of amorphous Mn-C alloys, as was done for Fe-C[1,2] and Cr-C[3] systems. To our knowledge, $\text{Mn}_{1-x}\text{C}_x$ amorphous films have never been elaborated. Sputtering is a powerful tool to obtain these alloys and their crystallization can produce new manganese carbides. Among the known manganese carbides, there are TPS carbides such as Mn_3C and Mn_5C_2 [4] and a TP chain carbide Mn_7C_3 . Mn_{23}C_6 and Mn_{15}C_4 were also mentioned [5]. Nearly all of the structure of these manganese carbides was established through the great similarity between Mn-C, Fe-C and Cr-C systems.

Experimental methods.

$\text{Mn}_{1-x}\text{C}_x$ amorphous films were deposited by RF magnetron sputtering onto glass slide substrates using a pure Mn target and variable Ar- CH_4 gas mixture as reactive plasma. The carbon and manganese content were determined by EPMA. The structure of as-sputtered films and their crystallization were studied by X-ray diffractometry using a Mo source, differential scanning calorimetry (DSC) and hot stage JEOL 200 kV transmission electron microscopy (TEM).

Results and discussion.

Depending on the CH_4 partial pressure, the carbon content of the films varies from $x = 0.13$ to $x = 0.37$. The X-ray analysis shows that when the atmosphere is CH_4 free, the film is composed of the fcc Mn_α phase without any preferential orientation. At a low CH_4 partial pressure, the film is composed of a solid solution of C in Mn_α . For $0.20 \leq x \leq 0.37$, the X-ray diffraction patterns (figure 1), selected area diffraction and bright field TEM observations show that an increase of carbon content render the films amorphous. Then, no trace of cristallinity could be detected, in any of $x \geq 0.20$ as-sputtered films, either by X-ray diffraction or by TEM.

Figure 1 X-ray diffraction profile ($\lambda_{\text{Mo}} = 0.07092 \text{ nm}$) of amorphous $\text{Mn}_{0.80}\text{C}_{0.20}$ film.

Figure 2 Formation temperature of manganese carbides as a function of x

The study of the stability of $\text{Mn}_{1-x}\text{C}_x$ amorphous alloys by means of DSC shows that the amorphous to crystalline state transition occurs as a direct transformation. Figure 2 shows the temperature T_0 of the carbide formation as a function of x , for amorphous samples heated at a rate of $83 \cdot 10^{-3} \text{ Ks}^{-1}$. This temperature shifts with carbon content. Thus, a maximum of T_0 exists around $x \approx 0.28$ and a minimum around $x \approx 0.34$. The same evolution was already observed for $\text{Fe}_{1-x}\text{C}_x$ alloys [2].

In the TEM, the samples are all heated with the same rate until crystalline phases are obtained.

Figure 3 TEM micrograph showing the feather shape morphology of TPS carbides and corresponding S.A.E.D obtained during the crystallization of a $\text{Mn}_{0.75}\text{C}_{0.25}$ amorphous film at 653 K.

For $x < 0.34$, feather-shaped carbides appear as shown in figure 3a and the S.A.E.D patterns obtained from these crystals often correspond to the same zone axis (figure 3b). This pattern is characteristic of TPS carbides when the electron beam is perpendicular to the TP sheets, but it is not

enough to determine which type of TPS carbides has been formed. For example, due to the similarity between Mn_3C and Mn_5C_2 , this pattern can correspond to a (001) Mn_3C zone axis as well as a (100) Mn_5C_2 zone axis. To know the linkage between the TP sheets, it is important to find the diffraction patterns which contain the direction called X^* perpendicular to these TP sheets. They are obtained on more crystallized films and the figure 4 shows a set of these S.A.E.D patterns. Some of them have already been observed for the iron carbides and they can be described with the help of two sets of diffraction spots:

- a first set of diffraction spots is characteristic of the TPS and their position are almost independent of the carbon content. They will be considered as invariant. A two dimensional basic reciprocal lattice which is common to all the S.A.E.D patterns - except this one of figure 4b - is drawn in figure 4e.

- a second set of diffraction spots is related to the linkage between the TP sheets and we can distinguish two cases :

- * This one for which the smallest distance between two invariant spots along X^* is divided in equal parts by 6 spots (figure 4a), 8 spots (figure 4b) and 1 spot (figure 4c). These distributions correspond to new carbon-rich periodic TPS carbides which are respectively Mn_7C_3 , Mn_9C_4 and Mn_2C . For the known Mn_3C and Mn_5C_2 carbides, this distance will be divided respectively by 2 and 4 spots [2]

- * This one for which the same distance is divided by four spots in five unequal parts. This kind of repartition corresponds to new one-dimensional aperiodic carbides for the Mn-C system. In this case, second set diffraction spots are regarded as satellites of first set diffraction spots and only one parameter δ is needed to explain the position of satellites with varying carbon content. With this description, some particular values of δ lead to a periodic structure (For example Mn_2C for $\delta = 0$, Mn_3C for $\delta = \frac{1}{3}$ and Mn_5C_2 for $\delta = \frac{1}{5}$). By measuring the δ value from the reciprocal plane of figure 4d ($\delta = 0.113$) and by interpolation between the previously particular δ values, it is possible to know the carbon content of this aperiodic TPS carbides which is $x \approx 0.31$. All these carbides can be described by chemical twinning [2].

Figure 4 A set of periodic (a,b,c) and aperiodic (d) TPS carbides S.A.E.D patterns obtained for different carbon concentration.

For $x \geq 0.34$, a new manganese carbide has been obtained (figure 5). It is a matter of the Mn_2C percarbide which is isomorphous with W_2C and Fe_2N [6] and for which C atoms are in octahedral interstices. The structure of this carbide is strongly dependent of the arrangement of C atoms and is hexagonal L'_3 type when these atoms are randomly distributed on the octahedral sites. Ordering of C atoms leads to superstructures. The diffraction pattern of figure 5b show diffraction spots characteristic of the L'_3 type structure, but also supplementary weak diffraction spots which can be interpreted with the orthorhombic ζ Fe_2N type structure. In addition, we can notice diffusion lines which only affect this orthorhombic structure [7]. A further heating permits a perfect ordered arrangement of this structure. Further investigation will be made for $x > 0.37$.

Figure 5 (a) TEM micrograph of Mn_2C crystal which often forms bend contour contrast. (b) S.A.E.D pattern and (c) its schematic representation showing spots due to both L'_3 and ζ Fe_2N type lattices.

Conclusion.

The crystallization mechanism of $\text{Mn}_{1-x}\text{C}_x$ amorphous films changes drastically at $x = 0.34$ and leads, in addition to the known TPS Mn_3C and Mn_5C_2 carbides, to new TPS carbides which can be periodic - thus we can detect Mn_7C_3 and Mn_9C_4 - or aperiodic and can reach the Mn_2C formula. For $x > 0.34$, a new Mn_2C percarbide is observed. This crystallization mechanism change which is correlated to a minimum of the crystallization temperature corresponds to a change in the C atoms sites : below $x = 0.34$, all the C atoms are in prismatic interstices and above this value the C atoms set into octahedral interstices. This change in C atoms sites, for the first crystallization products, suggests that there is probably a change in the local order of amorphous state for a characteristic carbon content $x = 0.34$. It is interesting to remark that it is possible to obtain two types of carbides - the TPS Mn_2C carbide and the Mn_2C percarbide for a same carbon content which is very close to 0.34.

References.

- [1] E.Bauer-Grosse, G.Le Caer : Mater.Sci.Eng, 99(1988)273.
- [2] E.Bauer-Grosse, G.Le Caer : Mater.Sci.Eng, 99(1988)31.
- [3] E.Bouzy, E.Bauer-Grosse, G.Le Caer : Mater.Sci.Eng, A133(1991)640.
- [4] K.kuo and Persson . J.Ir.Steel Inst : 39(1954)178.
- [5] J.P.Bouchaud : Ann.Chim., 2(1967)353 .
- [6] S. Nagakura, S.Oketani : Trans I.S.I.J, 8(1968)265.
- [7] A.Aouni and E.Bauer-Grosse : to be published.