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Short Communication

A New Example of Non-Crystalline Microstructure in Metallurgy

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Résumé. — Nous avons observé des particules de microstructures aperiódiques dans des aciers recuits. Les diagrammes de diffraction électroniques pris sur des petits domaines dans une particule sont ceux d'une phase cristalline alors que les diagrammes de diffraction pris sur l'ensemble de la particule ne sont plus périodiques. Nous interprétons cet effet par de la diffraction cohérente dans une microstructure de domaines cristallins séparés par des parois constitués d'une seconde phase. Les positions des pics de diffraction suggèrent qu'une phase quasicristalline icosaédrique est présente. Des études sont en cours pour examiner ce point.

Abstract. — We report on a non-crystalline microstructure encountered in particles that are formed during the annealing of some steels. The electron diffraction patterns taken on small areas are those of a crystalline phase but the diffraction patterns taken on larger area exhibit non-crystalline symmetry. These anomalous diffraction patterns are interpreted as the result of coherent diffraction between nanometer size domains. Observations show that a crystalline phase identified as a χ -phase structure is involved in this domain microstructure. Some of the electron diffraction pattern features suggest that an icosahedral phase might also be present. However investigations are under progress in order to check this point.

1. Introduction

This paper reports the existence of a microstructure exhibiting electron diffraction patterns inconsistent with the translation symmetry. This new example of non-crystalline symmetry does not correspond to a new aperiodical structure but to a complex microstructure. The anomalous behavior of the microstructure - which is revealed by the diffraction patterns taken in the transmission microscope on a rather large area ($0.2 \mu\text{m}$) - is not periodic. This aperiodicity is all the more unexpected since the diffraction patterns taken on very small area (less than 50 nm) are those of a crystalline phase.

The present communication aims at describing the diffraction patterns of this unusual microstructure. Though it is not possible yet to give a model of the structure, the position of the diffraction spots suggests the presence of an icosahedral phase.

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2. Aperiodicity in Selected Area Diffraction Patterns

Annealing of Fe-22Cr-5Ni-3Mo-0.03C duplex stainless steel in a temperature range between 650 °C and 750 °C produces the precipitation of very fine particles ($\approx 1 \mu\text{m}$) throughout the ferrite matrix. In the course of a transmission electron microscopy study, some of these particles have been noticed because of their remarkable behavior regarding electron diffraction patterns (Figs. 1 and 2).

The convergent beam electron microdiffraction shown in Figure 1 is obtained with a convergent electron beam focused onto the particle of interest. In this mode, the beam is characterized by a very small spot size (less than 50 nm) and a small convergence angle. Figure 1 shows that the particle is crystalline at a nanoscale and has a 4-fold symmetry axis. A full crystallographic analysis carried out with this microdiffraction mode shows that the structure is body centered cubic (cell parameter 0.89 nm) and belongs to the $I\bar{4}3m$ space group [1]. These crystallographic data are in agreement with a well known Frank-Kasper phase [2], the χ -phase (an isostructure of the α -manganese phase).

Electron diffraction patterns are then taken, on the same particles, but in the selected area electron diffraction (SAED) mode operating with an aperture whose diameter is 0.5 micron, i.e. about one third of the particle size. In this case, the SAED patterns (Fig. 2) are quite different from those obtained in the microdiffraction mode, even though they have been recorded along the same zone axes. For instance, the diffraction patterns shown in Figures 1 and 2a have been taken on the same particle with the same beam direction, only the size of the diffracting area has changed. Both diffraction patterns (Figs. 1 and 2a) exhibit a 4-fold symmetry but the spots in Figure 2a are not periodically arrayed.

The SAED patterns shown in Figures 2b and 2c have been taken on the same area as the diffraction patterns in Figure 2a but the sample has been tilted to other zone axes. These SAED patterns (Figs. 2b and 2c) correspond to $\langle 011 \rangle$ and $\langle 111 \rangle$ crystalline diffraction pattern, respectively, when the microdiffraction mode was used.

Analysis of the three SAED patterns shown in Figure 2 reveals some features which may also be recognized as non-crystallographic.

1) The diffraction spots on the 4-fold diffraction pattern (Fig. 2a) are no longer periodic. Only some diffraction spots can be indexed according to the χ -phase structure previously observed. These spots, which belong to the $\{033\}$ and $\{006\}$ types, are indicated by arrows

Fig. 1. — Microdiffraction zone axis pattern which shows that the particle has locally a periodic 4-fold diffraction pattern (cell parameter: 0.89 nm). For a full microdiffraction crystallographic study of these particles see Redjaimia and Morniroli [1].

Fig. 2. — Sequence of selected area diffraction patterns taken with an aperture of diameter 0.5 micron. The patterns have been recorded along the same zone axes as the diffraction patterns shown in Figure 1. The symmetry is preserved but the patterns are no longer periodic. In Figure 2a the spots are not periodically distributed. Note that, in Figures 2b and 2c, the spots exhibit anomalous splittings since they depend on the spot positions.

Fig. 3. — Outline of the diffraction pattern shown in Figure 2a. The size of the spot is related to the spot intensity. The grid recalls the position of the crystalline χ -phase spots.

on the diffraction pattern in Figure 2a. One of the $\{033\}$ spots corresponds to the spot E in Figure 3.

Besides, all spots do not have the same intensity. Long exposed electron diffraction patterns allow to identify a 4-fold motif build up with weak and strong spots. An outline of this pattern is given in Figure 3. Some remarkable ratios relate all these spot positions. The ratio of the reciprocal distances between the origin O and spots noted B, C and E (Figs. 2a and 3) is $OC/OB = 1.6$ and $OE/OB = 2.6$. In addition, the spots noted A and D correspond to the ratio $OD/OA = 2.2$.

2) In the diffraction pattern shown in Figure 2b, the anomalous behavior is not due to aperiodic spot positions but to spot splittings that depend on spot positions. Again no spot (except the $\{033\}$ χ phase spots) can be indexed with the χ -phase structure. However, if one considers the mean position of the diffraction spots, the diffraction pattern would be the $\{011\}$ zone axis diffraction pattern of the χ -phase crystal.

3) In the 3-fold SAED pattern shown in Figure 2c, most of the diffraction spots are also split. As in the previous pattern the splitting depends on the spot position. Again the mean positions of the split spots correspond to spots which can be indexed as χ -phase spots.

From the symmetry point of view, the SAED patterns displayed in Figure 2 show that the

crystallographic space group remains $\bar{I}43m$. Besides the aperiodicity of the SAED pattern, one must note that the diffraction spots are remarkably sharp. Only the weak spots in Figure 2a might show a little amount of diffuse scattering.

3. An Aperiodic Microstructure

The SAED patterns, when compared to the narrow beam diffraction patterns, raise two questions: 1) What is the origin of the aperiodicity? 2) Why have most of the diffraction spots of the χ -phase disappeared?

The occurrence of extra spots, satellites or spot splittings in diffraction patterns is a well-known effect in transmission electron microscopy. Extra spots or satellites might have different origins, for instance: a regular array of crystal defects, modulated structures or double diffraction. However, as long as the extra spots are generated by a periodic organization superimposed on a crystalline one, the resulting diffraction patterns are periodic. Spot splitting might also be due to the intersection of the Ewald sphere with diffuse scattering streaks located outside the diffraction planes. But, in this case, either the splitting is the same for each spot or there is a periodic relationship between the spot splitting and indexing. Consequently, our observations suggest that the present microstructure necessarily involves a non-crystalline organization along with the crystalline χ -phase domains revealed by the narrow beam diffraction.

Bright field images show that the particles have a complex microstructure characterized by a network of boundaries separating domains smaller than 100 nanometers. As a matter of fact, the density of boundaries and domains is too high for good conventional bright-field or dark-field imaging. High resolution electron microscopy (HREM) is here more adequate. The HREM image shown in Figure 4 was recorded along the 3-fold symmetry axis. It shows that the particle microstructure involves crystalline domains (size: about 20 nm) separated by thick walls. When the image is observed at glancing angle, one can note translation shifts and

Fig. 4. — High resolution electron microscopy image recorded along the 3-fold symmetry axis. The periodic domains are imaged while the structure between the domains is not yet resolved.

small misorientations between the crystalline domains. The period in the crystalline domains is measured to be approximately 0.6 nm, that is, consistent with the (011) χ -phase lattice spacing. Regarding the organization of atoms within the thick walls, our resolution is not yet good enough to image it properly.

The misorientations between the crystalline domains provide an understanding for the extinction of χ -phase spots on selected area diffraction patterns. As the wall domains do not show a particular organization, the aperiodic diffraction patterns should come from the structure of the phase constituting these walls. In other words, the crystalline χ -phase domains are probably separated by quasicrystalline phase walls. This hypothesis seems all the more natural since icosahedral phases have already been encountered in duplex stainless steels [3, 4] similar to the material on which the present observations have been made. In these steels, quasicrystals precipitate during high temperature annealing. They form either as micron-sized particles or as films wetting the interface between austenite and ferrite [5].

Some of the observations made on the selected area diffraction patterns are in agreement with the presence of an icosahedral phase.

a) The 6-dimensional cell parameter has been estimated to be $a_6 = 0.639 \text{ nm}^3$ on the basis of the electron diffraction pattern. As a matter of fact, the spot labelled E (Fig. 3) can be indexed as a (033) χ -phase spot (4.64 nm^{-1}) as well as a (2/4 0/0 0/0) diffraction spot of the icosahedral phase encountered in steels (4.63 nm^{-1} after [3]).

b) The ratios of the spot position measured on the 4-fold diffraction pattern have actually quite remarkable values ($\text{OC/OB} = 1.6$, $\text{OE/OB} = 2.6$, $\text{OD/OA} = 2.2$). They recall the values deduced either from the golden ratio ($\tau = 1.618\dots$ and $\tau^2 = 2.618\dots$) or from $\sqrt{5}$. It is a well-known feature of the icosahedral quasicrystals that the spot positions along 2-fold icosahedral axes follow a golden proportion while the ratio $\sqrt{5}$ is characteristic of the 5-fold icosahedral axes. In other words, it is possible to index the spots labelled A, B, C, D, E in the quasicrystalline system. As the spot labelled E can be indexed (2/4 0/0 0/0), the spots labelled B and C which are related to it by a golden ratio can be indexed (0/2 0/0 0/0) and (2/2 0/0 0/0).

c) The previous indexation of spots as 5-fold and 2-fold icosahedral directions means that in the present microstructure the (011) cubic direction is parallel to 5-fold and 2-fold icosahedral axes. This is consistent with the orientation relationship exhibited, in steels, by the icosahedral phase with the cubic matrix [3, 4]. This orientation relationship sets three (011) cubic directions parallel to 2-fold icosahedral axes while the three others (011) cubic directions are close to 5-fold icosahedral axes. It could also be described by one (111) direction parallel to a 3-fold icosahedral axis while the other three (111) cube axes are close to 2-fold icosahedral axes. This orientation relationship, though not the most frequent one, has already been encountered with other quasicrystals (Ti_2Ni for instance [6]).

Our diffraction observations are then supported by an interpretation in terms of a two-phase microstructure involving crystalline χ -phase and icosahedral phase domains. However since our HREM images are not sufficient to prove the existence of icosahedral phase within the walls, the remarkable ratios along the (011) directions are the strongest experimental points supporting our hypothesis. The fact that one finds, along a same (011) direction, diffraction spots coming from a 5-fold as well as a 2-fold icosahedral diffraction row shows that different variants allowed by this orientation relationship are present. This is a valuable piece of information because it indicates that the crystalline χ -phase might have been formed first and further generated the quasicrystalline phase.

This interpretation must be considered as a first tentative in this work. It needs to be confirmed by simulation of the diffraction of a crystal/quasicrystal microstructure. It is worth noting that modulated phases encountered in melt spun V-Co-Si alloys [7] show a strong

similarity with our particles. The spot shifts in melt spun V-Co-Si alloys are interpreted as a modulation effect. It is possible that the microstructure reported here constitutes an early stage in the formation of modulated phases similar to melt spun V-Co-Si alloys.

Simulation of the diffraction patterns are under progress with the help of the cut-and-project algorithm. Actually there are already examples of aperiodical microstructure generated by the cut-and-project method. Duneau [8, 9] has generated quasiperiodic geometrical models displaying microcrystalline structures. The geometrical approach generates, essentially, two types of microstructures: quasicrystalline domains separated by translation walls [9] and two-phase microstructures of quasicrystalline and crystalline domains. The former case agrees with the observed modulated phases [10] while the latter remains a theoretical construction. This theoretical two-phase microstructure is developed only for the octagonal tiling, a convenient example for 2-dimensional description. We then have to build this type of two-phase microstructure for the icosahedral case in order to compare with the experimental SAED patterns described here.

4. Concluding Remarks

Experimental diffraction patterns show the possibility of aperiodic microstructures which are periodic at the nanometer scale. We propose to interpret the aperiodicity as resulting from coherent diffraction between crystalline domains and quasicrystalline phase in the domain walls but this interpretation is still to be confirmed.

In any case, the absence of finite-size broadening of the diffraction peaks, in spite of the small size of the domains, shows the strong coherence between the crystalline domains and the phase within the walls. This coherence meets one of the major predictions of the aperiodic microcrystalline model [8]. The origin of such coherence and, in particular, its eventual link with the orientation relationships is of great interest concerning crystal/quasicrystal interfaces.

Finally, the present aperiodic microstructure being found in the χ phase, an isostructure of a very classical structure, the α -manganese phase, confirms again that non-crystalline organization is quite common in condensed matter.

References

- [1] Redjaimia A., Morniroli J.P., *Ultramicroscopy* **53** (1994) 305-317.
- [2] Frank F.C. and Kasper J.S., *Acta Cryst.* **11** (1958) 184.
The alpha-manganese structure is a famous exception to the Frank and Kasper rules. According to these rules, the local close packing condition is consistent only with some coordination numbers ($Z = 12, 14, 15$ and 16), the $Z = 13$ coordination number being forbidden. Among the 58 atoms of alpha-manganese cell, 24 of them have a $Z = 13$ coordination number.
- [3] Sidhom H. and Portier R., *Philos. Mag. Lett.* **59** (1989) 131.
- [4] Hu W., Jiang X.L. and Hsu S.S., *Philos. Mag. Lett.* **61** (1990) 115.
- [5] Sidhom H., Bonnet S. and Portier R., "Quasicrystals and Incommensurate Structures in Condensed Matter", M.J. Yacaman, D. Romeu, V. Castano and A. Gomez Eds. (Singapore: World Scientific, 1989) p. 478.
- [6] Zhang Z., Kuo K.H., *Philos. Mag. B* **54** (1986) L-83.
- [7] Lu G. and Feng Y.C., *Philos. Mag. B* **62** (1990) 563.
- [8] Duneau M., *J. Phys. I France* **1** (1991) 1591.
- [9] Duneau M., *J. Phys. I France* **2** (1992) 1731.
- [10] Menguy N., Audier M. and Guyot P., *Philos. Mag. Lett.* **65** (1992) 7.