Acta Microscópica, Vol. 4, N° 1. May. 1995, p. 21-31

TRANSMISSION ELECTRON MICROSCOPY STUDY OF THE GAMMA PHASE OF THE Cu-Al SYSTEM.

Gabriel Torres-Villaseñor[1], M. Avalos-Borja[2], C. Piña-Barba[1]
1. Instituto de Investigaciones en Materiales UNAM, Apdo P. 70-360, México D.F.04510, México
2. Instituto de Física, Laboratorio de Ensenada B.C. México 02732.

ABSTRACT

The g-phase region of the Cu-Al binary system for aluminium concentrations between 30,8 and 38,5 at % was studied by transmission electron microscopy (TEM). The observations revealed the presence of inversion anti-phase domains (IAPD). The domains form regular arrays in two distinct configurations a) triangular domains with boundaries parallel to {112} planes and b) ribbon domains parallel to {110}. This IAPD structure was observed for alloys composition intermediate between those corresponding to P-type and R-type γ-brass. The transition from one IAPD configuration to the other is described and the changes in mechanical properties were studied by micro-hardness measurements.

KEY WORDS

Inversion Domains. Antiphase *boundaries. Mechanical properties of gamma (Cu-Al).*

INTRODUCTION

1. Structural Considerations

According to recent binary phase diagram [1], the structures of phases at 30 to 42 at % Al, γ_1, δ, and γ_o (Murray's notation) are based on the γ-brass structure. The structure of γ- brasses is often described as a simple array (e.g. bcc, CsCl or fcc) of complex clusters of atoms. These 26-atom clusters are constructed as successive enveloping polyhedral starting with an inner tetrahedron (IT) surrounded by an outer tetrahedron (OT) itself by an octahedron (O) and finally a cubo-octahedron (C.O.) consisting of 12 atoms as shown in Fig 1. These more or less spherical clusters, are arranged somewhat like giant "atoms" on a cubic lattice.

In the γ(Cu-Al) the clusters are arranged in the CsCl structure and thus contain clusters with two different compositions (P-Type). The resultant structure (space group P43m) is complex cubic of the γ- brass type containing 52 atoms per unit cell, based on a 21/31 electron compound. The homogeneity range of the undistorted cubic phase extends from 31,3 to 35,2 at % Al. The unit -cell edge *increases from 0,87 to 0,8715 nm between* these composition limit [2].

As aluminum replaces copper over this phase range, some of the positions allotted to copper become occupied by aluminium atoms. The observed [3] x-ray intensity changes show that aluminium atoms replace copper on the group of atoms that lies on the planes of symmetry. Thus, at a composition corresponding to $Cu_{17}Al_9$ (34,6 at. % Al) this group contains two copper atoms less than at the composition Cu_9Al_4 (30,8 at % Al). The stoichiometric composition of this last phase, is inside of the two phase field. The remaining groups are not affected by the change of composition. At even higher aluminium content (38,3-40,2 at % Al) a third phase δ was found; it is a rhombohedrally deformed modification of the γ phase with a lattice parameter equal to 0,8704 nm and $\alpha = 89°8$. The structure of its high-temperature form γ_0, which is stable between approximately 1063 and 1373 k, is not well known.

2. Inversion Domains.

An inversion boundary is an interface separating two regions consisting of structures which are related by an inversion operation [4]. Between the regions on either side of the boundaries no intensity difference will be observed in bright field (BF) whatever the diffraction conditions, but in multiple beam situations pronounced contrast can be produced in the dark field (DF) image for certain diffraction conditions. Serneels et al.[5] showed that for those diffracting vectors which do not reveal the non-centrosymetric nature of the crystal, the domain boundaries will be imaged as stacking faults if symmetry axes in the two domains do not coincide.

It is the purpose of this work to use DF imaging techniques for obtain information on the γ(Cu-Al) phase structure and their defects, and to find out how this structures affects the mechanical properties of the alloy.

MATERIALS AND METHODS

Cu-Al alloys in the composition range between 30 and 40 at % Al. were prepared by melting 30-g charges of the appropriate amounts of copper an aluminum using a tungsten arc furnace under an argon atmosphere. The copper and aluminum were analytical quality in sheet form from Baker Analysts. For homogenization, the alloys were annealed at 1120 k, for 24 h. A group of specimens containing all the prepared compositions, was quenched in air and another group was very slowly cooled in the furnace. Vickers hardness measurements were taken in each specimens.

Specimens for transmission electron microscopy were prepared by jet electron polishing in a mixture of 10% perchloric acid an 90 % ethanol at about 280 k .

RESULTS

Alloys with compositions between Cu_9Al_4 (30,8 at% Al) and $Cu_{17}Al_9$ (34,6 at.% Al) air quenched ,were examined by transmission electron microscopy (TEM). All of the specimens give the same diffraction pattern, typical for P-Type γ-brass. Fig. 2. The lattice parameter "a" equal to 0,87 nm is in agreement with the value reported in the literature. Characteristic for this composition range was a low concentration of lattice defects; only a few antiphase boundaries with the appearance of stacking faults, could be observed an identified. Fig. 3.

Specimens with a slightly higher aluminium content (34,6- 35 at. % Al) did not show any detectable difference in the diffraction pattern compared with that of the cubic γ- phase. By direct imaging in the electron microscope, however, we found a high concentration of defects with the characteristic imaging properties of inversion boundaries. Typical configuration are shown in Fig.4. The micrograph is a bright-field image taken in two-beam conditions with a beam direction close to [110]. The diffraction patterns of the alloy containing these domains were indistinguishable from those of the usual γ-brasses structure, there being no observable extra diffraction spots or streaking associated with the presence of the domains. Figure 5a and 5b shows bright and dark-field images in a multibeam situation. Figure 5a is a multiple beam bright fiel image, no contrast was observed between domains. Figure 5b was taken using the (3,5,3) reflection, this gave pronounced black and white contrast between alternate domains . No difference in intensity between adjacent domains was observed in any bright-field images. In a study of the γ phase in Cu-Zn, Morton [6], has also observed triangular configurations of inversion-related domains. Similar configurations can be detected in this Cu-Al system, as is evident from Fig. 5.

If the aluminium of the alloys becomes more than 35 at % Al, the diffraction pattern changes. Typical (110), section is shown in Fig. 6. The basic spots reveal satellites associated with a long-period modulation parallel to the (1,-1, 0) planes. This modulation agree to 20 times the distance between (110) planes, that is 12,32 nm. Direct imaging in a bright field gives evidence for a periodic array of lattice defects Fig. 7. From observations on the various stages of formation of this long- period super-structure it could be identified as a long-period stacking of inversion boundaries (LPIB). Small local differences in the composition, can produce de coexistence of triangular IAPD structure and LPIB structure as is shown in Fig 8.

The spacing of the satellites in the diffraction patterns becomes larger the larger the aluminium content until the aluminium content reaches 38 at. % Al. Near 38 at. % Al the superstructure disappears. This means that the period of the superstructure decreases until it reaches a critical point where a transformation occurs.

In specimens with a composition between 35 and 38,1 at % Al which are very slowly cooled (6 °C/h) from 700 °C, no long-period superlattice is present. We found two different phases in this material: one is P-Type γ-brass an the other is R-type γ-brass. In the R-type γ-brass region, twin boundaries parallel to a (0,1,-1) plane are observed as shown in Fig. 9. Coherent twin boundaries in (0,1,-1) planes are observed as straight lines separating areas of different shades.

Hardness Measurements.

Fig. 10 shows the results of the Vickers hardness measurements. The hardness increases with the aluminium content, and reaches a maximum around 35 at. % Al.. It is notorious that in this region the slowly cooled specimens shows a minimum hardness in contrast with the quenched specimens that shows a maximum. The hardness values become the same in quenched and slow cooled specimens when the aluminum content is increased.

DISCUSSION

When the aluminium content is increased in the alloy the composition changes continuously from Cu_9Al_4 to $Cu_{17}Al_9$, at this composition the first Brillouin zone of γ-brass which is limited by planes of the type (330) and (411) is completely filled [7]. If we add aluminium to the alloy, some electrons have to be transferred in to the second zone. this increases the total energy of the system. To create more electron places in the first Brillouin zone, the volume of the zone has to increase by introducing some modifications the structure. This is in agreement with our experiments; between 30,8 and 34,6 at % Al, only pure P-type γ-brass exists. At higher concentrations of aluminium this structural change is realized by a high density of inversion domains.

At higher aluminium contents, the alloy

develops a superstructure. This seems to be the mechanism to keep the γ-brass stable at e/a (electron concentration) values higher than the ideal value. The superlattice only appears for e/a values between 1,69 and 1,76. At higher aluminium concentrations the superlattice disappears. The decrease in the period with increasing aluminium content is also in agreement with the predictions of Sato and Toth [8].

For e/a values between 1,76 and 1,82 the rhombohedrally deformed modification of γ(Cu-Al) is stable. This confirms the hypothesis of Brandon et al. [9]. They explain the presence of an R-type γ-brass in some alloy systems to be responsible for the fact that g-brasses are stable at higher concentrations than are γ-brasses with a cubic structure.

The big difference in hardness found between the quenched and slowly cooled material, at the composition close to 35 at % Al, could be due to a decomposition into two phases of this alloy. One part of the crystal is copper rich and forms pure P-type γ-brass; the other part is aluminium rich and forms the R-type γ-brass structure. To explain this phenomenon, we assume that the long-period superlattice is not the stable configuration at room temperature. If the crystal is allowed to reach a state of minimum energy, decomposition occurs. This gives a crystal with a much lower concentration of defect planes than in the long-period super-structure. This is perhaps the reason why the crystal decomposes.

CONCLUSIONS

The g region of the Cu-Al system was reinvestigated by transmission electron microscopy and electron diffraction. In specimens quenched from 1120 k and with an aluminium content between 34,6 and 38,1 at % Al a long-period structure was detected. In slowly cooled specimens of the same composition a decomposition into P-Type and R-type γ-brass takes place. This different microstructures originates strong differences in hardness of the material.

AKNOWLEDGEMENTS.

The autors thanks Mr. A. Caballero for his help in preparing the illustrations of this work.

REFERENCES

1. Murray J.L. (1985) Int. Met. Rev. **30(5)**

2. Westman S., (1965) Acta Chem. Scand. **19:** 1411-1418

3. Bradley A.J., Goldschmidt H.J. and Lipson J., (1938). J. Inst of Met., **53:** 149-162

4. Snnykers M., Serneels R., Delavignette R., Gevers R. and Amelinckx S. (1962) Phys. Stat. Sol. **2:** 636-642.

5. Serneels R., Snykers M., Delavignette P., Gevers R. and Amelinckx S. (1973) Phys Stat. Sol. (b) **58:** 277-281

6. Morton A.J. (1975) Phys. Stat. Sol. (a), **31:** 661-673

7. Rayne J.A. (1980) "Theory of Brillouin Zones", Westinhouse Research Laboratories **Ch.5:** 210-219

8. Sato H. and Toth S. (1961) Phys. Rev., **124:** 1833-1845

9. Brandon J.K., Pearson W.B., Riley P.W., Chieh C. and Stokhuyzen R. (1977) Acta Crystallogr.,(B) **33:** 1088-1095

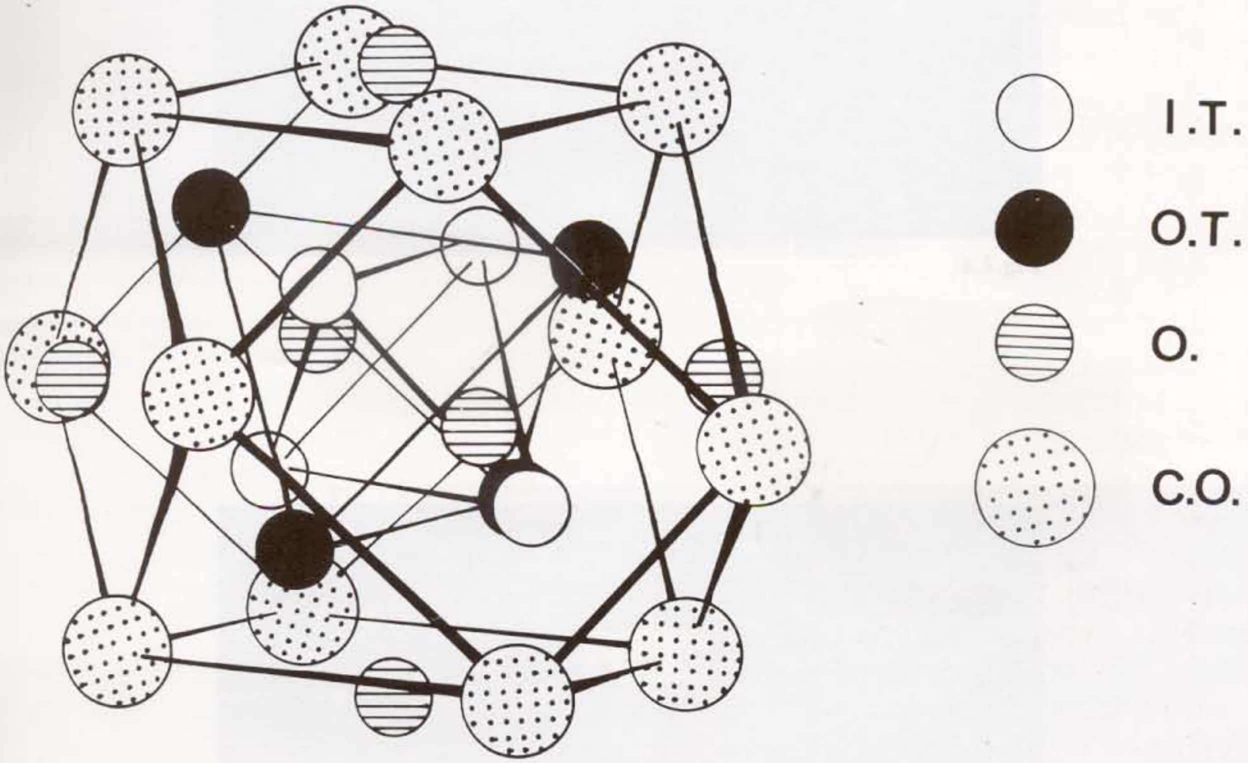

Fig. 1. Cluster of 26 atoms appearing in the structure description of γ-brasses .IT, inner Tetrahedron; OT outer tetrahedron; O, octahedron; CO, cubo-octahedron.

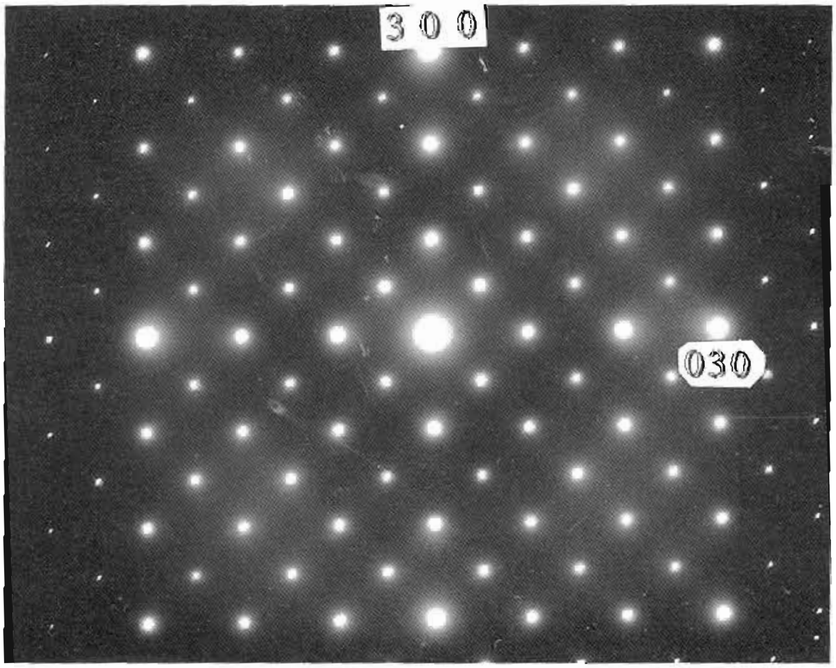

Fig.2.a

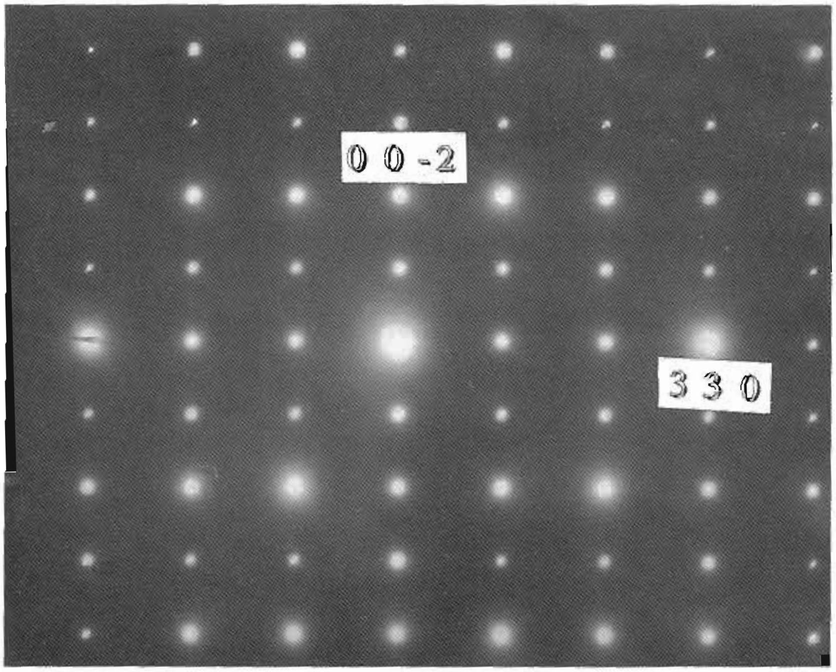

Fig.2.b

Fig.2. Diffraction patterns of Cu_9Al_4 specimens along different zones identifying the P-typeγ-brass structure: (a) (100) ; (b) (110).

Fig.3.a

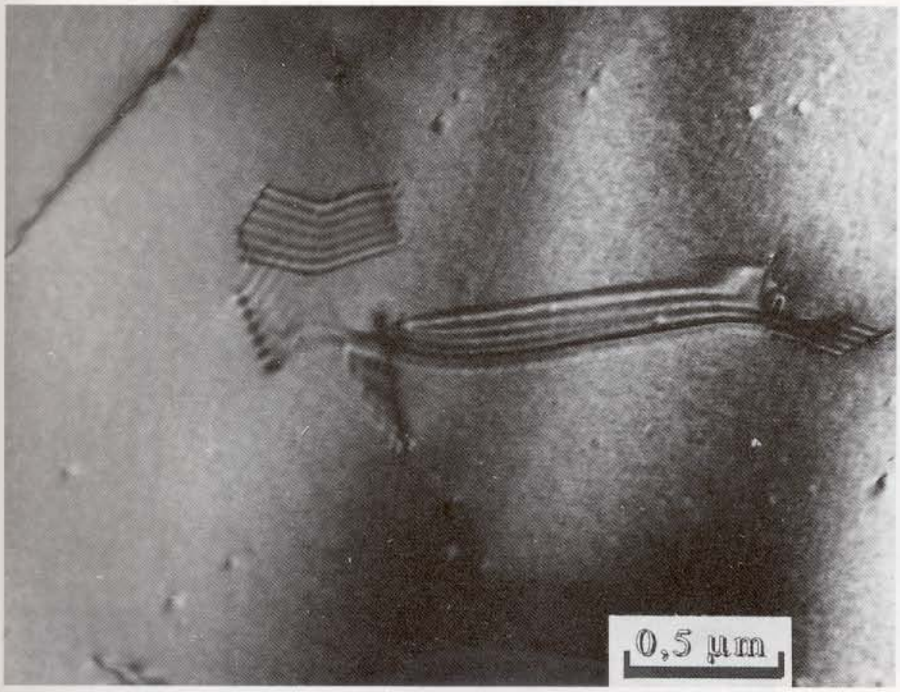

Fig.3.b

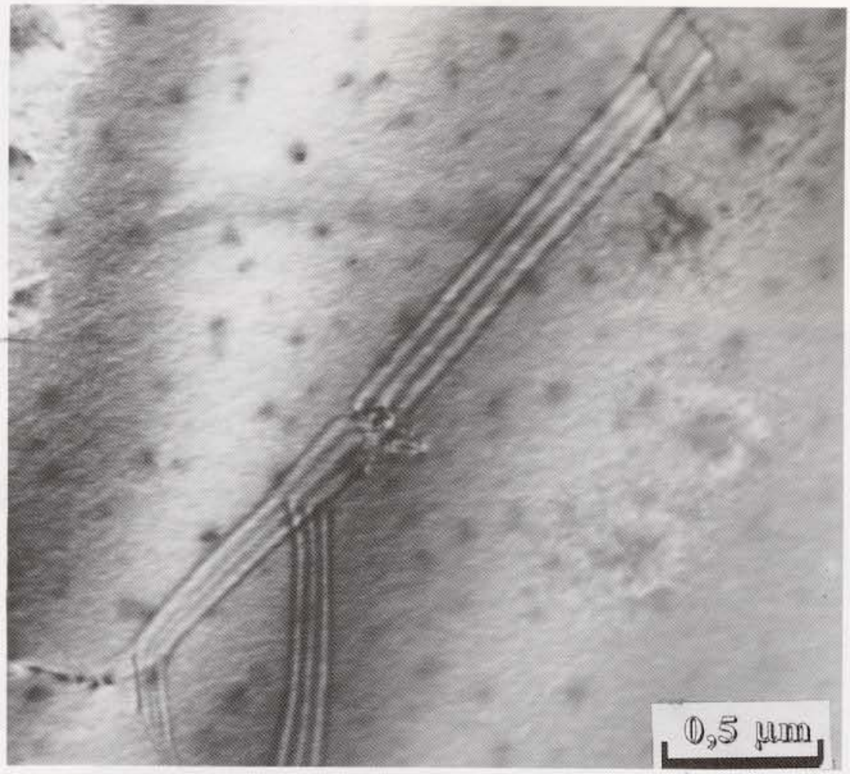

Fig.3. Antiphase boundaries attached to a dislocation, (a) Cu-31,5 at % Al; (b) Cu-33 at % Al.

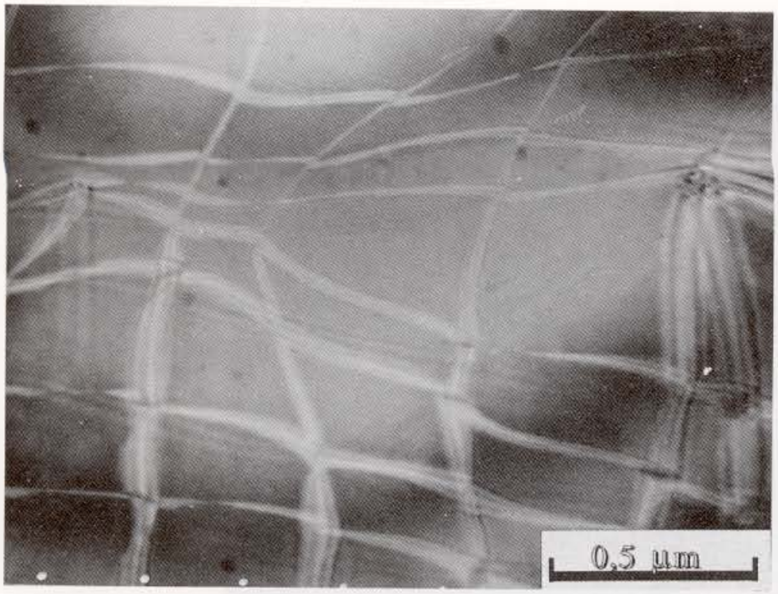

Fig.4. Bright-field micrograph showing a coarse network of anti-phase inγ(Cu-Al) of composition Cu-35 at % Al. Note the formation of nodelines along which several boundaries intersect.

a

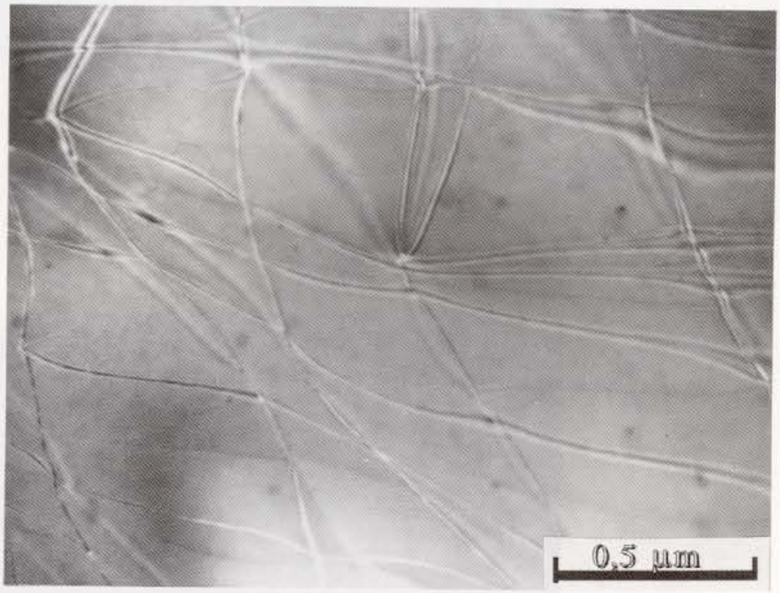

Fig.5.b

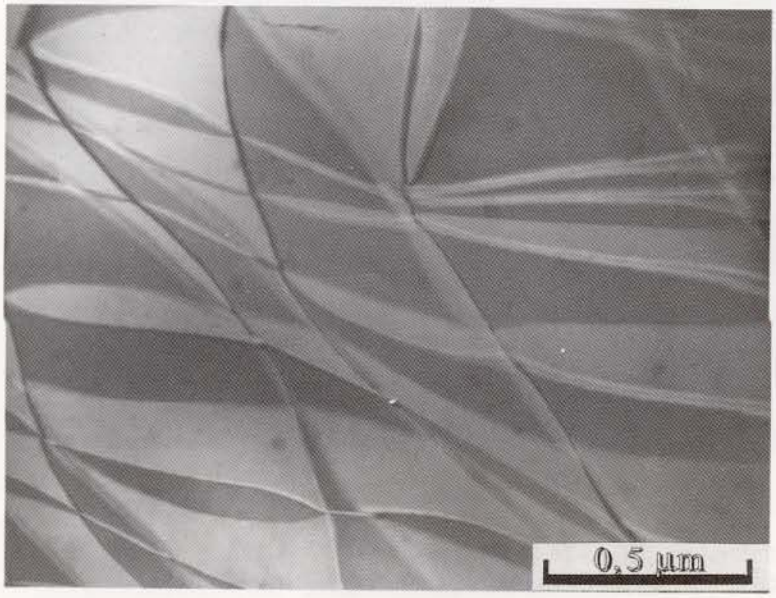

Fig.5. (a) Multiple beam bright field image, note absence of contrast between domains. (b) Multiple beam dark field image, using the (3,5,3) reflection, note pronounced contrast.

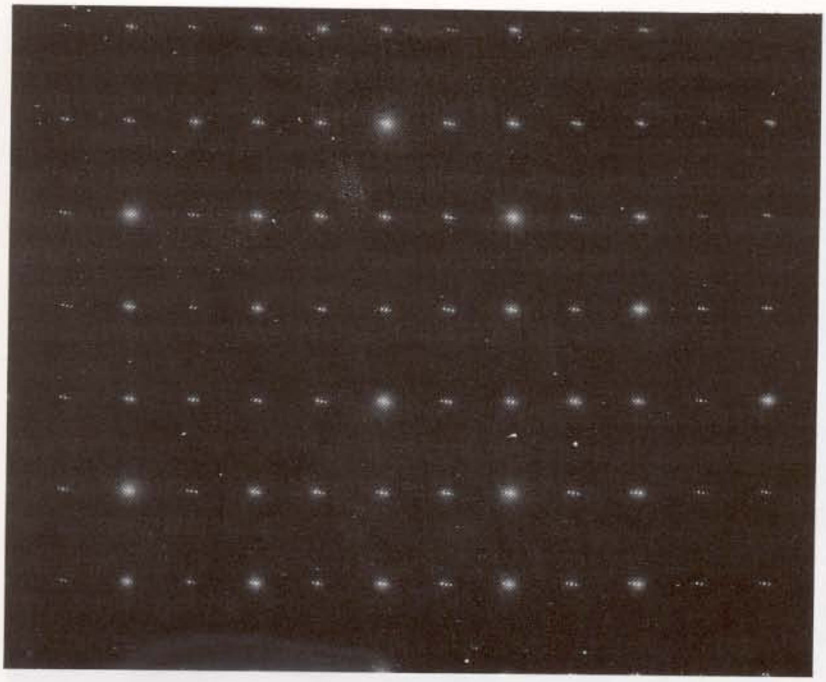

Fig.6. A (110) diffraction pattern of specimens with composition Cu- 35 at % Al showing the spot splitting due to the formation of an LPIB structure.

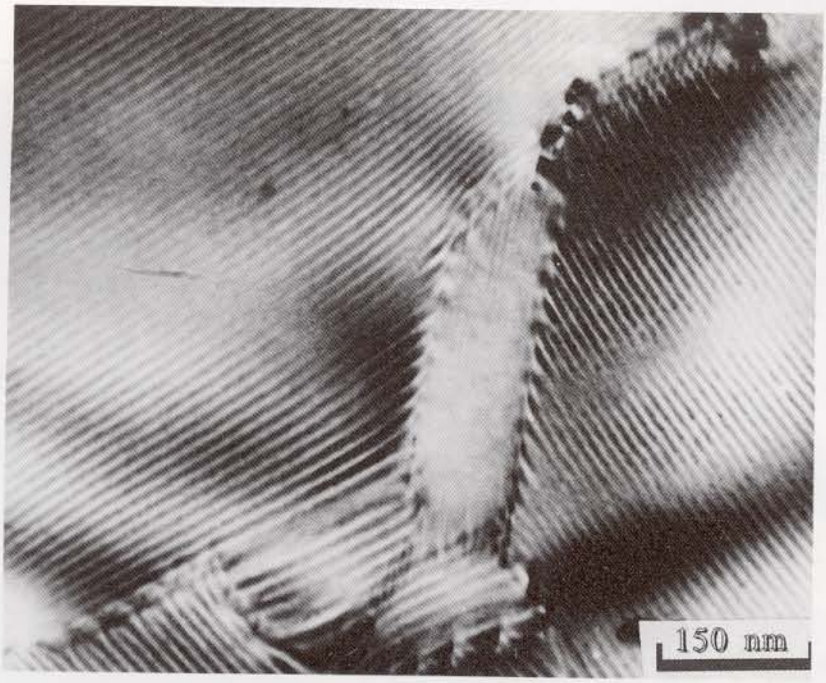

Fig.7. Bright field image of the LPIB structure. The distance between a dark and bright lines of the superlattice corresponds to 20 times the distance between (110) planes of the cubic γ-phase.

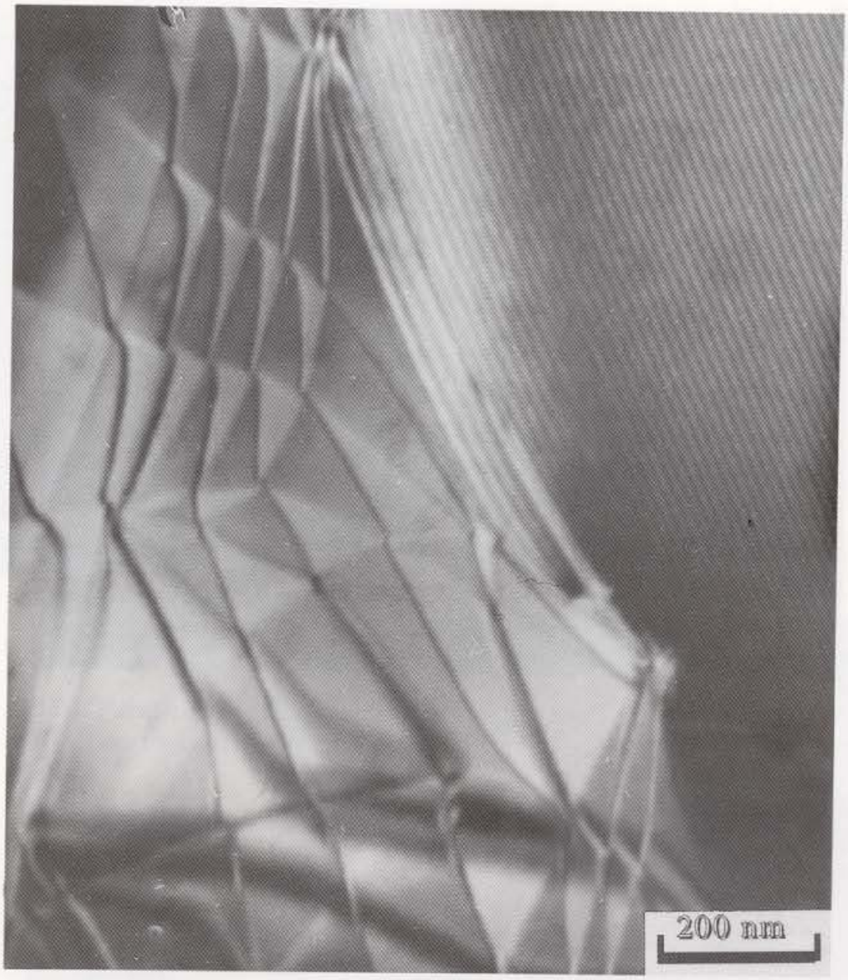

Fig.8. Micrograph showing a region of triangular inversion domains coexisting with a LPIB structure.

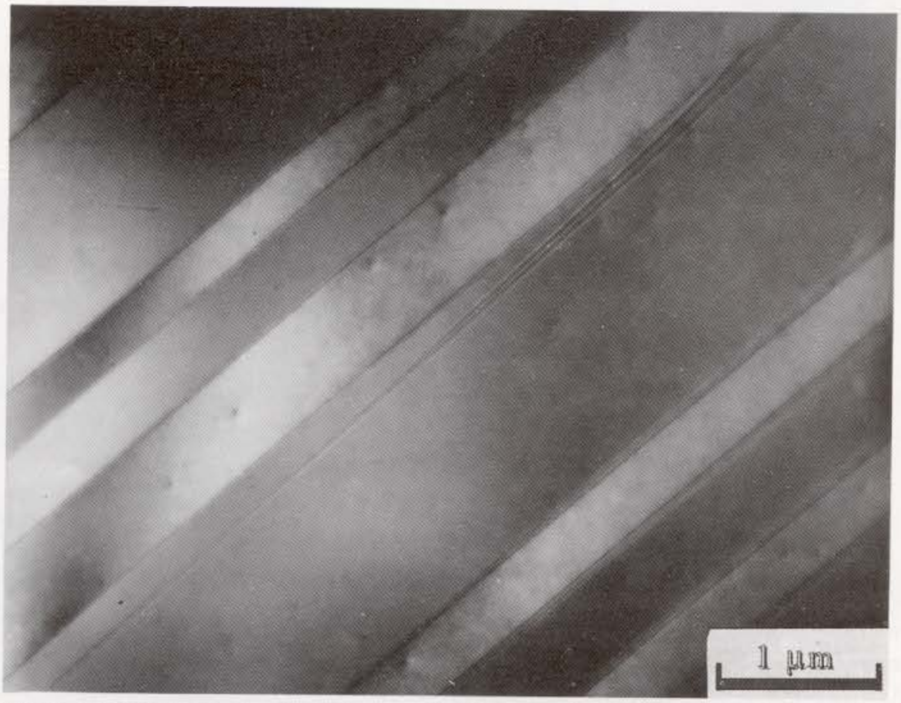

Fig.9. Twin domain structure observed in the very slowly cooled specimens with composition Cu-35 at % Al.

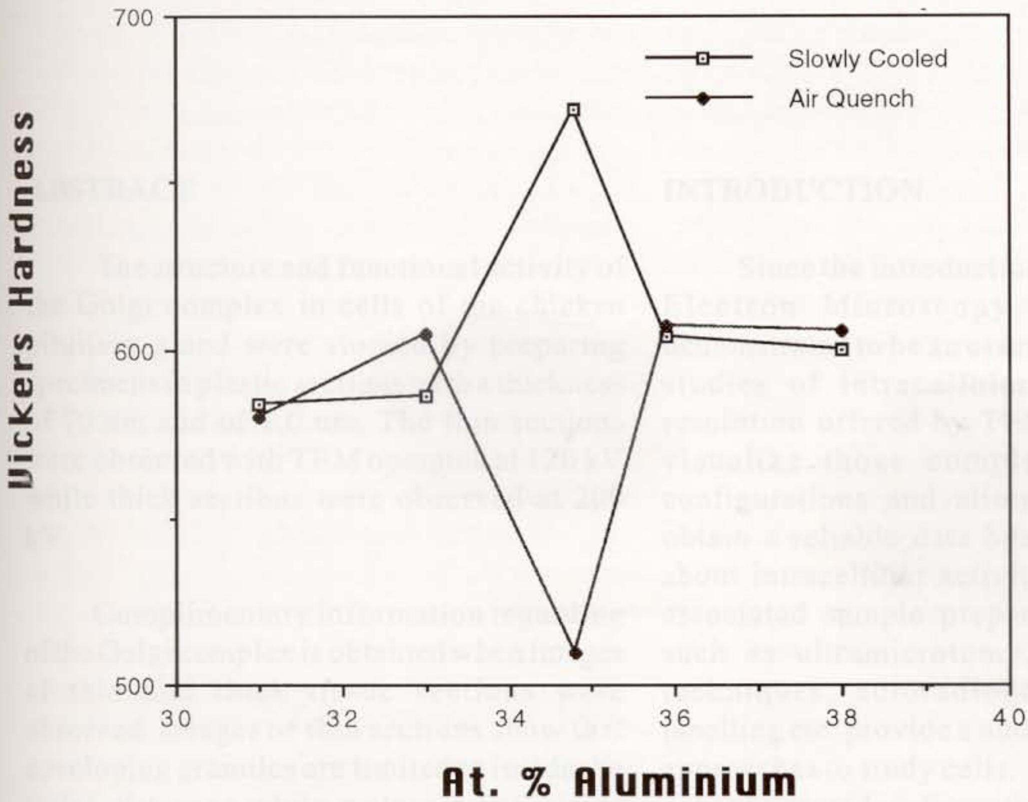

Fig.10. Influence of the composition and thermal treatment on the hardness of the γ(Cu-Al). A big difference in hardness values is observed at the 35 at % Al.