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STRUCTURAL STUDY OF AMORPHOUS $Al_{0.20}As_{0.50}Te_{0.30}$, $Al_{0.10}As_{0.40}Te_{0.50}$ AND $Al_{0.10}As_{0.20}Te_{0.70}$ BY X-RAY DIFFRACTION (I)

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An analysis of the atomic radial distribution function of $Al_{0.20}As_{0.50}Te_{0.30}$, $Al_{0.10}As_{0.40}Te_{0.50}$ and $Al_{0.10}As_{0.20}Te_{0.70}$ amorphous alloys obtained from quenching of the molten mixture of the elements was performed. A structure in which all the Al atoms are tetrahedrally bonded to the other types of atoms in the material, would satisfy the requirements of the experimental curve. Tetrahedral groups might be linked to each other by As and Te atoms, or directly through a Te or As atom belonging to more than one tetrahedra.

1. Introduction

The switching effect has been observed in several alloys of the system of Al-As-Te amorphous alloys and their crystallization characteristics seem to depend strongly on the composition, especially on the Al content [1-3]. A structural study of the whole amorphous formation zone has been undertaken in order to help to understand the thermodynamical behaviour of these alloys.

Here we report the results of an X-ray radial distribution analysis of $Al_{0.20}As_{0.50}Te_{0.30}$, $Al_{0.10}As_{0.40}Te_{0.50}$ and $Al_{0.10}As_{0.20}Te_{0.70}$ alloys. Short-range structure models are proposed on the basis of the knowledge of other Al-As-Te amorphous alloy system compounds.

2. Experimental

The samples used were obtained from commercial Al, As and Te of 99.99% purity. Appropriate proportions of elements were sealed in a quartz ampoule under a neutral Ar atmosphere and then melted. The molten mixture was rotated for four days inside a furnace at temperatures above 800°C and quenched in liquid nitrogen.

The bright metallic solid obtained from quenching was ground to a fine powder (< 325 mesh) which was compacted by pressure into a brick of

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Table 1
RDF characteristics

	Alloy					
	$Al_{0.20}As_{0.50}Te_{0.30}$		$Al_{0.10}As_{0.40}Te_{0.50}$		$Al_{0.10}As_{0.20}Te_{0.70}$	
Maximum	1	2	1	2	1	2
Position (Å)	2.55	3.95	2.61	3.95	2.67	4.05
Limits (Å)	2.10–3.00	–	2.20–3.05	–	2.25–3.05	–
Area (at.)	2.36	9.69	2.36	8.36	2.04	6.95
Error	±0.1	±0.2	±0.1	±0.2	±0.1	±0.2
Density ($g\ cm^{-3}$)	4.89 ± 3%		5.15 ± 3%		5.38 ± 3%	

approximately $30 \times 12 \times 1$ mm^3. No sign of crystallinity appeared in a conventional X-ray diffraction experiment.

The diffraction intensities were measured on a Norelco diffractometer equipped with a bent graphite monochromator, scintillation counter and standard electronics. The radiation used was MoK_α ($\lambda = 0.71069$ Å).

Four series of data were collected in the interval $7 \leqslant \leq 2\theta \leq 110°$, two in increasing angles in 2θ and the other two in reverse. From 7° to 70°, step sizes of $(2\Delta\theta) = 0.2°$ were used and from 70° to 110° $(2\Delta\theta) = 0.5°$. Times were measured by keeping a fixed number of counts.

The intensity assigned to each observation point was the mean value of those measured at that point. Most of averaged values lie within 3% of the average with a maximum deviation of 5%. The densities of the materials measured with a pycnometer are shown in table 1 with an estimated error of 3%.

3. Radial distribution functions

The observed intensities were corrected for background, polarization, multiple scattering and normalized into electron units (e.u.) by the high angle method and then, the incoherent scattering was subtracted.

The radial distribution function (RDF) is calculated as:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + rG(r), \tag{1}$$

where ρ_0 is the mean atomic distribution over the sample which was directly deduced from the experimental density; $\rho(r)$, the local atomic density which is affected by the Fourier transform of the $f_i f_j/(\Sigma x_i f_i)^2$ products and $G(r)$ is

$$G(r) = \int_0^{s_{\max}} F(s) \sin(sr)\, \mathrm{d}s \tag{2}$$

being

$$F(s) = si(s) \quad \text{and}\ i(s) = \frac{I_{\text{e.u.}} - \sum x_i f_i^2}{\left(\sum x_i f_i\right)^2}, \tag{3}$$

where x_i is the atomic fraction of the ith element, with i = Al, As, Te; and $I_{\mathrm{e.u.}}$ represents the resulting intensity values after corrections.

The $F(s)$ function was theoretically extended to $s_{\max} = 30$ Å^{-1}, to avoid spurious oscillations in $G(r)$ below the first significant maximum due to the lack of high s data, by the method described in ref. [4].

The RDFs after theoretical extension of the experimental data have been plotted in fig. 1.

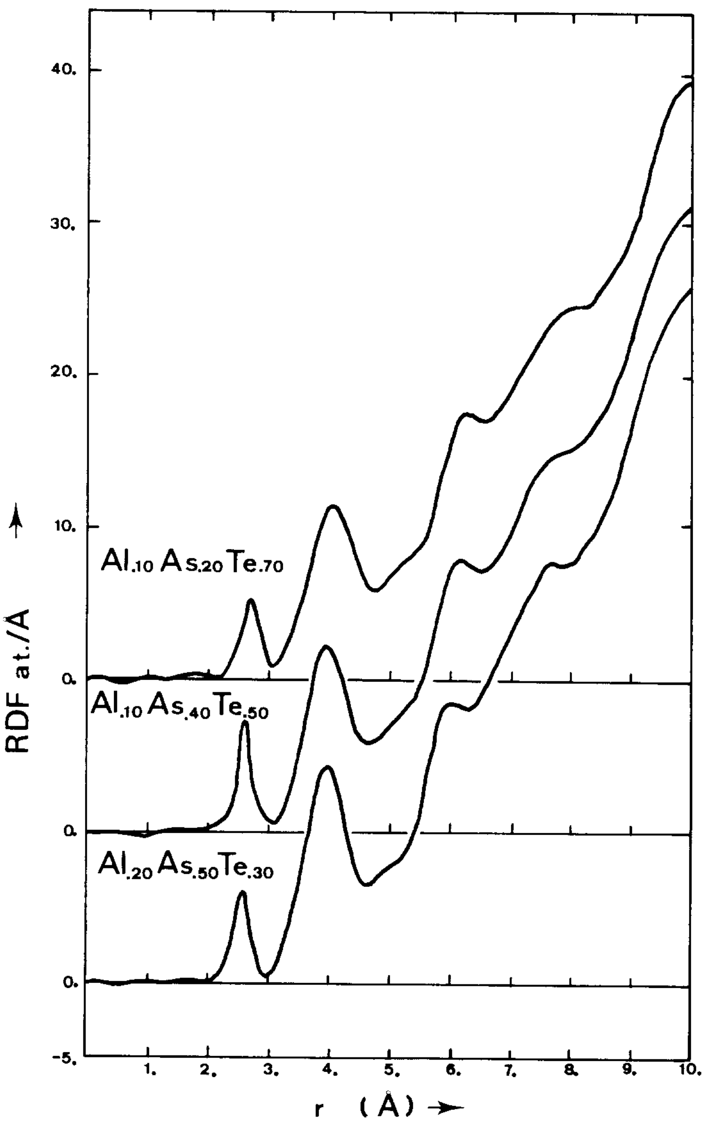


Fig. 1. Radial distribution functions.

All the calculations were made at the Computation Centers of the Instituto Hidrográfico de la Marina and the Centro de Investigaciones Técnicas de Guipuzcoa, with programs written by D'Anjou and Sanz [7].

4. Results and discussion

The analysis of experimental RDFs and density of each compound may be summarized by the values given in table 1.

The area under the first peak was calculated by means of Simpsom's formula and those beneath the second ones, with the method proposed by Stesiv [8], errors were estimated.

The general features which show the RDFs of these amorphous compounds are very similar to those found in earlier works about the radial distribution analysis of alloys of the Al–As–Te amorphous alloy systems [4–6]. The outstanding difference is the absence of a small peak, present in $Al_{0.23}Te_{0.77}$ [4] as well as in $Al_{0.20}As_{0.40}Te_{0.40}$ alloys [5], around $r = 3.5$ Å.

Overlapping between the first and second coordination spheres which hinders the accurate calculation of the number of first neighbours is observed for all our alloys, just as occurs in compounds of As–Te amorphous alloy systems [9].

In all the cases we considered, we found that the first maxima were wide enough to prevent us from discarding any possible bond as can be seen in table 1.

The area under the first maxima is related to the main structural parameters by the expression:

$$\begin{aligned} A = \frac{1}{\pi}\sum_{i,j} x_j \frac{n_{ij}}{r_{ij}} \Bigg\{ & \left(A_{0ij}s_{\mathrm{m}} + A_{1ij}\right)\frac{\cos s_{\mathrm{m}}a'_{ij} - \cos s_{\mathrm{m}}b'_{ij}}{s_{\mathrm{m}}} \\ & + A_{0ij}L\frac{|a'_{ij}|}{b'_{ij}} + r_{ij}A_{1ij}\int_{b'_{ij}}^{a'_{ij}} \frac{\sin s_{\mathrm{m}}x}{x}\,\mathrm{d}x \\ & + r_{ij}\left[A_{0ij}\left(\frac{1-\cos s_{\mathrm{m}}b'_{ij}}{b'_{ij}} - \frac{1-\cos s_{\mathrm{m}}a'_{ij}}{a'_{ij}}\right)\right]\Bigg\}, \end{aligned} \tag{4}$$

after results obtained by Vázquez and Sanz [10] deduced from the linear regression fitting of the $f_i f_j/(\Sigma x_i f_i)^2$ products versus s, over the tabulated angle interval. A_{0ij} and A_{1ij} are the coefficients in the fitting.

r_{ij} represent the standard first neighbour distances between two different atoms and $a'_{ij} = a - r_{ij}$ and $b'_{ij} = b - r_{ij}$ where a and b are the lower and upper limits of the first maximum respectively.

n_{ij} are the averaged numbers of i-type atoms in the first coordination sphere of a j-type atom and s_{m} represents the maximum value of s for which the atomic scattering factor is tabulated [11]. In this work $s_{\mathrm{m}} = 18.85$ Å^{-1}.

To calculate the n_{ij} parameters four hypotheses have been formulated following some already proved criteria in previous work dealing with compounds of Al–As–Te amorphous alloy systems [3–5]. These hypotheses are:

(1) We may suppose that the number of Al–Al bonds is negligible by taking into consideration its low bonding energy with regard to the other pair bonding energies (table 2) and the low atomic proportion in the material.

(2) We suppose tetrahedral coordination for Al atoms just like in crystalline compounds of this element with As or Te [17,18] and in amorphous $Al_{0.23}Te_{0.77}$ [3].

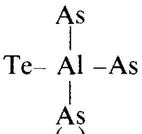
(3) The bonding situation may be formally regarded as if each Al atom took one electron from one of the As or Te atoms which surrounds it, making a sp3 tetrahedral hybridation. The atom which gives the electron becomes fourfold or threefold coordinated depending on whether it is an As or a Te atom.

On the other hand, we have no criterion to assign which of the As or Te atoms gives one electron to Al in every tetrahedra. We suppose, consequently, that every atom in the tetrahedra vertex provides $\frac{1}{4}$ of an electron (in a probabilistic sense) to the Al atom.

(4) Furthermore, the existence of As_2Te_3 units and Te free chains (only for the $Al_{0.10}As_{0.20}Te_{0.70}$ alloy) is proposed.

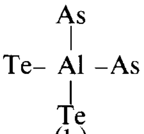
4.1. Short-range structure of $Al_{0.20}As_{0.50}Te_{0.30}$ alloy

If the aforesaid bonding scheme is kept, the average number of Al–Te bonds forming these tetrahedral basic units should be of 1.5 which could be interpreted, for instance, as if these were two types of tetrahedra:



$$\begin{array}{c} \mathrm{As} \\ | \\ \mathrm{Te}-\mathrm{Al}-\mathrm{As} \\ | \\ \mathrm{As} \end{array}$$

(a)



$$\begin{array}{c} \mathrm{As} \\ | \\ \mathrm{Te}-\mathrm{Al}-\mathrm{As} \\ | \\ \mathrm{Te} \end{array}$$

(b)

in the suitable proportions to give this mean value.

Table 2
Bond strengths

Bond	Bond strength (D°/kcal mol.$^{-1}$)	Ref.
Al–Al	36.7 ±3.4	[13]
Al–As	69.77±2.95	[a]
Al–Te	64.0 ±2.3	[14]
As–As	91.3 ±2.5	[15]
As–Te	77.48±1.35	[a]
Te–Te	63.2 ±0.2	[16]

[a] Obtained using Pauling's formula [17].

Another interpretation could be to suppose tetrahedra centered in one Al atom and surrounded by Te or As exclusively, both units being in appropiate amounts.

In the former interpretation, for 100 atoms of material, there would be 10 of each type of tetrahedra.

Under these conditions, if every atom has its bonds satisfied, we will be able to calculate all the n_{ij} structural parameters in terms of an indeterminate number of As–Te bonds per 100 atoms of material, which we call α.

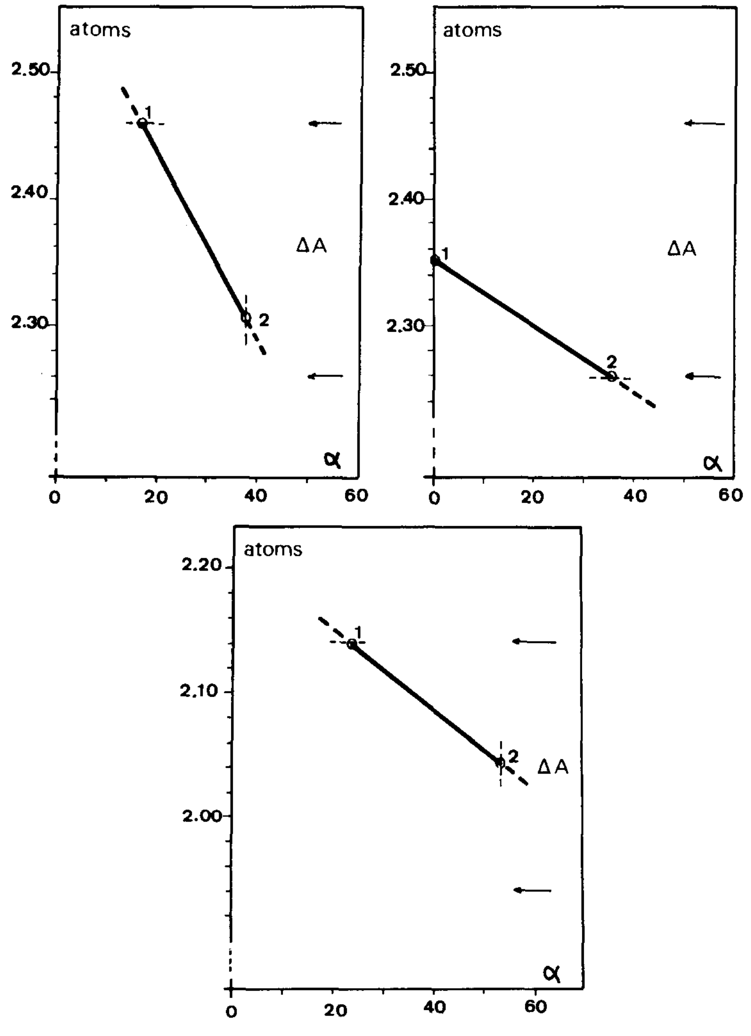


Fig. 2. Theoretical area beneath first maximum versus number of As–Te bonds in every 100 atoms of material (α). (a) $Al_{0.20}As_{0.50}Te_{0.30}$ (b) $Al_{0.10}As_{0.40}Te_{0.50}$ (c) $Al_{0.10}As_{0.20}Te_{0.70}$. ΔA represents the area error.

The first maximum area may be expressed after eq. (4) as:

$$A = 2.57 - 6.95 \times 10^{-3}\,\alpha, \tag{5}$$

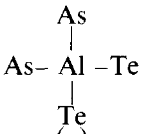
which is plotted in fig. 2a. Only the portion of line within the error estimates limits for the area, and without negative values of n_{ij} parameters, has been drawn. Thus, the structural models stay indeterminate between two limiting situations (shown by 1 and 2 in fig. 2) which essentially differ in the quantity of As–Te bonds formed.

This quantity varies from 15.9 to 37.5. The increase of As–Te bonds is carried out at the expense of the decrease on As–As and Te–Te bonds. These go from 48.3 and 10.8 respectively for case 1 to 37.5 and 0 for case 2, always for an hypothetical material sample of 100 atoms.

Theoretical calculation of the first peak position has been carried out for both extreme values of α, resulting in $r = 2.59$ Å and $r = 2.57$ Å for cases 1 and 2 respectively. That is why we think case 2 to be the most probable. Tetrahedra units would be linked either by means of As–As or As–Te bonds. The absence of Te–Te bonds is noticeable, at least in order to affect basically the mean structure of the material.

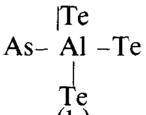
4.2. Short-range structure of $Al_{0.10}As_{0.40}Te_{0.50}$ alloy

For this compound, the average number of As atoms surrounding one Al atom after hypothesis (3) is 1.78. So, we may represent this situation as if there were two types of tetrahedra units like the following ones:



$$\mathrm{As{-}\overset{\displaystyle As}{\underset{\displaystyle Te}{Al}}{-}Te}$$

(a)



$$\mathrm{As{-}\overset{\displaystyle Te}{\underset{\displaystyle Te}{Al}}{-}Te}$$

(b)

In every 10 tetrahedra there would be 8 of type (a) and 2 of type (b).

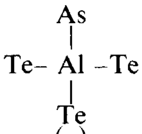
In the same way as before, the area beneath the RDFs first peak has been calculated as an α parameter function (number of As–Te bonds in every 100 atoms of material). The resulting expression is:

$$A = 2.36 – 2.80 \times 10^{-3}\alpha$$

and its graphical representation is on fig. 2b. Taking the experimental area value and its error limits into consideration, the plausible interval for α is between $\alpha_1 = 0$ and $\alpha_2 = 35.7$. The corresponding theoretical first peak positions are 2.68 Å and 2.67 Å respectively. The experimental result is $r = 2.61$ Å. On principle, all models are possible. But as no As–Te condition is requested for case 1, we think case 2 is closer to the real situation than the first one is.

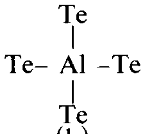
4.3. Short-range structure of $Al_{0.10}As_{0.20}Te_{0.70}$ alloy

If supposition (3) is to be kept, the average quantity of As atoms surrounding one Al atom in every tetrahedra is 0.89. This is compatible with a configuration consisting of the following two tetrahedral basic units:



$$\begin{array}{c}\mathrm{As}\\ | \\ \mathrm{Te{-}Al{-}Te}\\ | \\ \mathrm{Te}\end{array}$$

(a)



$$\begin{array}{c}\mathrm{Te}\\ | \\ \mathrm{Te{-}Al{-}Te}\\ | \\ \mathrm{Te}\end{array}$$

(b)

There would be 9 of type (a) and 1 of type (b) in every 10 tetrahedra. Calculation of n_{ij} structural parameters gives rise to the equation:

$$A = 2.21 - 3.13 \times 10^{-3}\alpha.$$

The extremal valid values of α are 22.4 (case 1) and 53.3 (case 2), fig. 2c. Both resulting theoretical first peak positions are similar (2.73 Å). It seems logical to take an intermediate value of α for discussion. For this situation, 7.7 and 49.5 are the number of As–As and Te–Te bonds, respectively, in every 100 atoms of material.

This result shows an appreciable number of As–Te and Te–Te bonds and a low number of As–Te bonds. It may be proposed that some tetrahedral units are linked by means of the remaining As or Te not tetrahedrally coordinated, in such a way that As–As bonds are almost completely avoided.

5. Conclusions

All these structures may be described as a complicated tridimensional framework of covalent bonds tetrahedrally orientated around the Al atoms. The first neighbours of Al atoms are As or Te atoms. The number of Al–As and Al–Te bonds are proportional to the relative concentrations of As and Te elements. Tetrahedra can connect either directly through an atom which is bonded with more than an Al atom or by means of As or Te atoms by way of a bridge. For the $Al_{0.10}As_{0.20}Te_{0.70}$ alloy, the existence of Te chains is possible too. These chains may probably be forming a separated phase.

The amount of As–Te bonds in every 100 atoms of material remains undetermined. This quantity decides, especially in $Al_{0.10}As_{0.20}Te_{0.70}$ alloy, the existence or not of a separated phase. The only experimental parameter to check is the area beneath the RDF first maximum. The theoretical value for this area has been calculated from the n_{ij} parameters which do not distinguish a continuous amorphous structural model from another containing separated phases. Hence, this analysis does not permit us to discard either of these two possibilities.

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