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producida por D.M. Pasquevich y F. Lovey

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SALIÓ

Structural and Microstructural Changes in Zirconia in Dilute Chlorine Atmosphere.

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Abstract:

The tetragonal-to-monoclinic phase transition in zirconia powders when exposed to various gas mixtures was studied. Analysis was done at 940°C in the presence of argon and different chlorine-argon mixtures. X-ray diffraction shows that the phase transition is accelerated in the presence of Chlorine. Transmission Electron Microscopy reveals changes in the microstructure of the particles subjected to the gaseous mixtures.

1. Introduction

The stable crystalline form of zirconia at room temperatures is monoclinic. Above 950°C this structure transforms into body-centered tetragonal; at still higher

temperatures, the stable phase is cubic. The monoclinic-to-tetragonal transition is of martensitic character, and the tetragonal phase cannot be retained by quenching. Nevertheless the tetragonal phase is ocasionally observed at room temperature. This peculiar form of metastability has been studied by several authors. Since the paper by Garvie[1] to date, numerous articles have dealt with this subject. However it has not been possible to establish the reasons of its appearance with certainty. Garvie[1] and other authors [2 - 7] indicated that the stabilization of the tatragonal phase at low temperatures might be due to a particle-size effect, on the grounds that the surface energy of this phase is lower than that of the monoclinic phase. Some investigators[8] considered that since the transformation is martensitic, the stabilization might be due to mechanical tensions in the particles. Other authors [8,9,10] attributed the metastability to a structural similarity between the amorphous precursor and the tetragonal phase. It has also been advanced that impurities or defects might retain the high-temperature phase [12,13].

Murase and Kato[6] found that the tetragonal to monoclinic transition is accelerated by the presence of water vapour in the gas phase. In our laboratory we found differences in the transformation velocity in zirconia powders heated in dry air and oxygen, the transformation being faster in air. These results led us to investigate the effect of a chemically more agressive

atmosphere. Chlorine diluted in argon was chosen for this purpose. The study was made using X-ray diffraction, transmission electron microscopy (TEM) and thermogravimetry (TG).

2. Experimental Procedure.

The study was performed on polycristalline zirconia (*) of better than 99.8% purity, initially containing 54% monoclinic phase, and a specific area of 4.5 m^2/g, as measured by nitrogen adsorption at 77 K.(**)

Zirconia samples were prepared from amorphous zirconium hydroxide obtained by ammonia hydrolysis of $ZrCl_4$ (***) after the technique described by Yani et al. [9]. To obtain structural standards, of the samples thus prepared, one was transformed into pure tetragonal zirconia, by heating the hydroxide in air at 400°C; another was calcinated at 800°C to obtain the monoclinic variety.

These two samples were used to determine the electron diffraction patterns of both pure phases, and served as standards for the identification of the mixed phases in the rest of the samples.

The commercial zirconia samples were placed in a quartz crucible in the center of a tube of the same material, through which a slow flow of either Ar or

Ar-Cl_2 mixture with a partial pressure of 300 torr Cl_2. Each sample was kept at 100°C for one hour and was then placed in a tubular furnace preheated to 940°C. The samples reach the working temperature in about 8 min. They are kept at the experimental temperature for the selected time, and are then quenched.

Thermogravimetric studies were effected on the samples using a Cahn 2000 thermobalance (#) and a gas control line [14] under the same experimental conditions as above, viz. 940°C and 300 torr chlorine partial pressure. The resolution of the TG system under these conditions is 10 micrograms, the sample size being of about 2 mg.

The phases present in the thermally treated samples were determined by X-ray powder diffractometry, with Ni-filtered radiation (##). The relative amounts of the monoclinic phase was calculated from the equation [15]:

$$\text{Monoclinic phase (\%)} = \frac{\left[I_m(111) + I_m(11\bar{1})\right] \times 100}{I_t(111) + I_m(111) + I_m(11\bar{1})}$$

where $I_m(111)$ and $I_m(11\bar{1})$ are the diffraction intensities of the (111) and $(11\bar{1})$ planes of the monoclinic phase, and $I_t(111)$ is the intensity of the (111) planes of the

tetragonal phase.

The same samples subjected to XRD where studied by Transmission Electron Microscopy (TEM) (###). To this end they were dispersed in water, and a droplet was dried on a copper-mesh screen.

3. Results.

1. Thermogravimetry. The TG runs showed that neither of the samples exposed to either Ar or Ar-Cl_2 mixtures suffered mass losses during thermal treatment.
2. X-Ray Diffraction analysis: The XRD allowed us to follow the phase transformation in time. Results are shown on Fig. 1, on which the relative content of the monoclinic phase is shown as a function of time at the experimental temperature for the samples exposed to the different atmospheres. Is is easy to see that in the presence of chlorine the transformation is much faster than in pure Argon.
3. Transmission Electron Microscopy: a. The initial powder consisted of policrystalline particles of irregular shapes and sizes ranging from 1 micrometer to 50 nm approximately. Some isolated larger particles up to about 50 micrometers were also observed. Since the XRD of this powder showed the presence of about 54% of the monoclinic structure, the rest being tetragonal, the phase distribution was studied by the diffraction and

dark-field modes. Some of the particles were composed of very small domains (in general less than 15 nm) of the tetragonal phase (see fig 2(a)). The monoclinic phase was found in rather larger domains of about 0.1 to 0.2 micrometers. This is shown on Fig. 2(b). (For comparison, all photographs have the same magnification).

Changes in powders annealed in Ar atmosphere:

After annealing at 940° during 1 hour (sample A1 on Fig 1) the XRD of the powder showed the presence of about 80% of the monoclinic phase. The observation by TEM indicated changes at the edges of the particles; the crystallites appear larger than initially and they are freer, maintaining only partial surface contact with one another (Fig 3(a)). Most of these partially separated crystallites have a monoclinic structure (Fig 3(b)). The tetragonal phase seems to be present in the smallest domains near the particle edge. No information on the phase composition of the thicker part of the particles could be obtained by this technique. Some large domains with tetragonal structure can also be observed, as shown on Fig 3(c). There is evidence that the particles begin to disaggregate through this edge effect. The crystallites with monoclinic structure separate completely from the initial powder particles as can be seen on Fig 3(d).

The powder annealed for longer periods under similar conditions (up to three Hours, sample A2 on Fig 1) showed

similar characteristics as those seen in sample A1, except for a more pronounced disaggregation.

Changes after annealing in Ar-Cl_2

The TEM showed two main differences with the samples annealed in pure argon:

i) The crystallites are, on the average, from 5 to 10 times larger and are completely monoclinic.

ii) The tendency to disaggregate the original particles by loosening the individual crystallites or clusters from the edge, is rather more pronounced in this case.

These two characteristics are clearly seen in Figs 4(a) and (b). The crystallites on Fig 4(b) are all monoclinic single crystals. Notice the polyhedral shapes of these particles.

4. Discussion.

The observation of the original zirconia powder indicated that the particles contained both phases. As was already pointed out by Mitsuhashi *et al* [8], the phase transition of these particles is more difficult than that of single-domain particles, due to the fact that the grain boundaries act as a barrier against the propagation of the phase transformation. This is due to the martensitic nature of the t -> m transition. The change involves a modification of the shape and volume of the transforming domain, which introduces tensions and

deformations in the neighboring domains, which can eventually crack the particle apart. These events are the reason that these transformations of a polycrystalline particle are normally not as fast as could be expected for a true, unhindered martensitic transition. Transformation speed is in this case determined by the rate with which these inhibiting tensions can relax. The results of our experiments are in accord with these considerations. The TEM analysis indicates the appearance of a large number of isolated crystallites in the samples treated in both Ar and Ar-Cl_2. These crystallites are not seen in the original powder; they form during thermal annealing, probably by loosening from the larger particles. This diaggregation is induced by internal strains due to the transformation of the tetragonal domains. Similar results have been found in other systems by various authors, as described in a recent review by Chupakhin et al. [17].

On the other hand, the results found in the presence of the Ar-Cl_2 atmosphere indicate that the presence of chlorine favors the t -> m transition, as is clearly seen on Fig 1. In the presence of this gas, both the domains and the isolated crystallites grow more than in pure Ar, it is clear that one of the effects of chlorine is to enhance the mass transport in the oxide. Murase and Kato [4] have already pointed out that the presence of water vapour enhances surface transport, and other authors [5, 6, 16] have shown that the t -> m transformation involves crystallite growth of both phases. The observation of

our sample B shows that both the domains and individual crystallites have grown to 5 to 10 times more than in sample A1 for equal annealing times. A comparison of the sizes of the crystallites liberated in Ar (about 15 nm) with those obtained in the presence of Cl_2 (about 30 to 100 nm) again shows that mass transport is enhanced in the corrosive atmosphere.

An observation of the shape of the single crystals shown on Fig 4(b) leads to the thought that this is a direct consequence of the disaggregation of particles with no further growth, since otherwise one could have expected more rounded shapes, and not sharp edges similar to those seen in the domains which form part of the larger particles. A comparison of Figs 4(a) and 4(b) shows the similarity between the sizes of the isolated crystallites and those bound in larger particles. This likeness suggests that the final size of these single crystals may have been reached at a time when they were still bound in larger particles, and not by growth at a later time. The larger numbers of these isolated crystallites formed in the presence of Cl_2 suggests that the rupture is more intense in this case. It is is possible that this effect might be explained as pointed out by Hirth and Rice[18], considering that the adsorption of chlorine on grain boundaries or interphases might degrade cohesion and may lead to intergranular separation. In the same sense, it was already pointed out by Petch [19] that gas adsorption affects the propagation of cracks by diminishing the fracture

stress.

Considering that both the surface area of the samples(4 m^2/g) and their mass (ca. 2 mg) are quite small, this adsorption cannot be determined by our TG equipment. However, another effect of the adsorption is the increase in surface diffusion which manifests itself in the enhanced growth of the crystal domains in the chlorine atmosphere. The adsorbed molecules change the energy and the distribution of the different surface sites, and act as a directing force for surface mobility. This mechanism is consistent with the fact that at low temperatures zirconia surfaces are active, and their behavior in the nucleation is affected by this surface mobility[20]. We can thus discard the possibility of a mass transport mechanism through the gas phase. Under the experimental conditions, the only reasonable process that might generate a gaseous species is the following,

$$ZrO_2 + 2\ Cl_2 \longrightarrow ZrCl_4 + O_2$$

but at 940°C, $\langle G^\circ \rangle$ = + 32.035 Kcal/mole [24], so that this reaction is quite unfavourable thermodinamically. Our TG results, in which no mass change is observed, also are evidence that no gaseous species are produced by the interaction of Cl_2 with the oxide.

5. Conclusions.

The results of this work indicate that in the

presence of both an inert gas, or Ar - Cl_2 phase transition is accompanied by the growth of the domains of both phases, and by the disaggregation of the oxide particles. In the presence of Cl_2 these effects are enhanced and occur faster.

The growth of the domains in the presence of Cl_2 correlated with a larger surface mobility. The increase in the rupture of the material is caused by the interaction of the gas with the grain boundaries, which is thermodinamically favoured by the adsorption on the fresh surfaces thus originated. Since we are in presence of a phase transition which is kinetically controlled by the building up and relaxation of internal tensions, both the decrease of the interphase area through domain growth and the rupture of the particles are controlling factors in the transformation. The low plasticity of the material leads to tension relaxation through rupture.

The mentioned effects explain the role of the atmosphere and the temperature, and suggest that the tetragonal phase may exist in metastable form in small domains which build large, compact, particles.

(*) (Koch-light Labs., Ltd.)

(**) (M 2205 Micromeritics Instrument Corp.

(***) (Fluka AG)

(#) (Cahn Instruments, Inc.)

(##) (Philips PW 1310/01)

(###) (Philips EM 300)

Figure Captions

Fig 1. Effect of the thermal treatment on the tetragonal to monoclinic transition at 940°C in different atmospheres.

Fig 2. Microstructure of the initial powder. Dark field electron micrograph showing: a. tetragonal and b. monoclinic domains. Enclosed, the respective electron diffraction patterns.

Fig 3. Microstructure after annealing in Ar atmosphere. a. bright field showing separation of the crystallites at the edges. b. Dark field of monoclinic crystallites. c. Dark field of tetragonal crystallites. d. Isolated crystallites, disaggregated from larger particles.

Fig 4. Microstructure after annealing in Ar-Cl_2 atmosphere: bright field electron micrographs. a. The edge of a large particle showing disaggregation. b. Isolated monoclinic crystallite with polyhedral shape.

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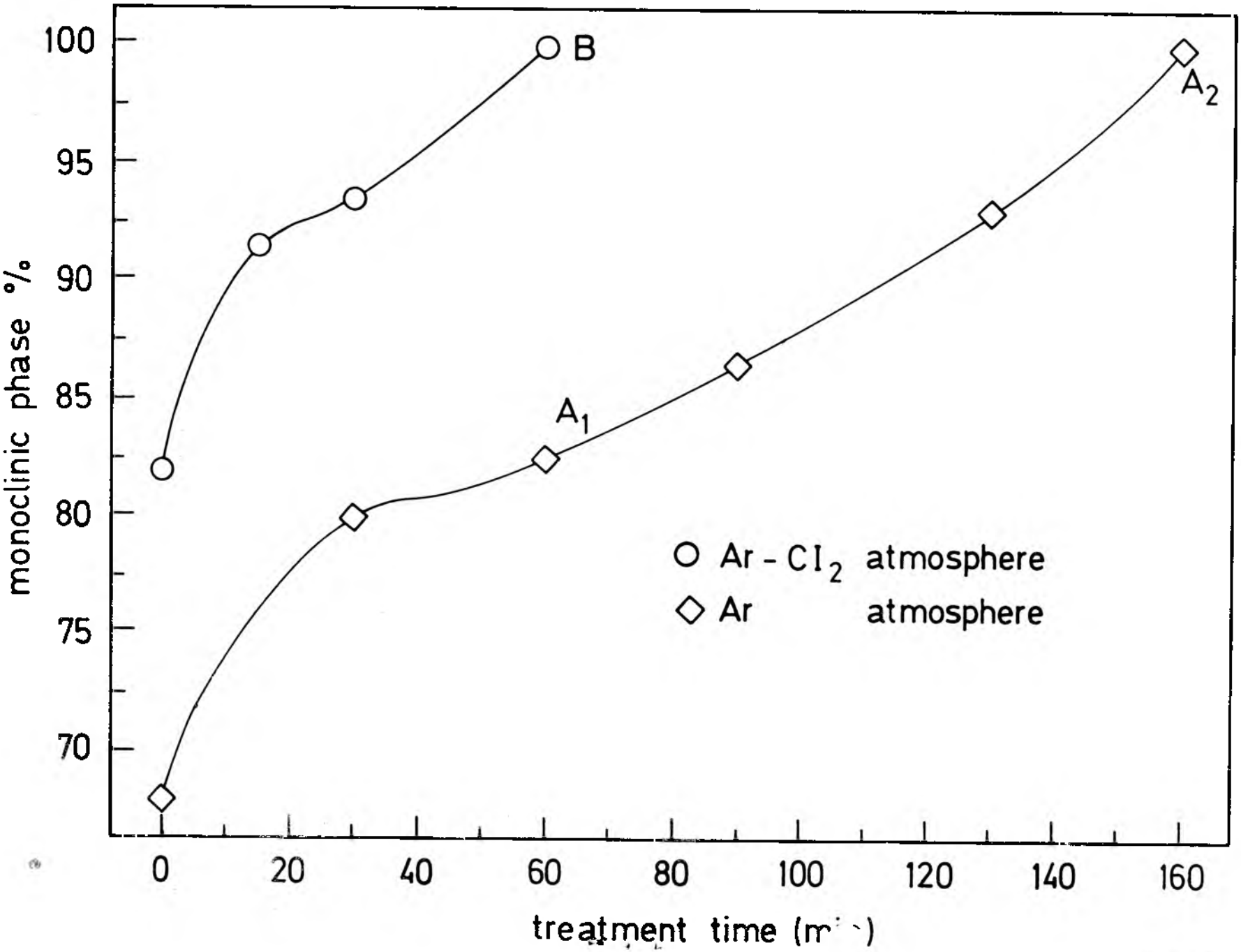
100
95
90
85
80
75
70
monoclinic phase %
B
A1
A2
Ar - Cl2 atmosphere
Ar atmosphere
0
20
40
60
80
100
120
140
160
treatment time (min)

S.C. DE BARILOCHE, 11 MAYO 1988

SEÑOR DIRECTOR DEL CENTRO ATOMICO BARILOCHE:

De acuerdo con las normas establecidas para la publicación de trabajos (RAR 96/78), elevo para su consideración el trabajo titulado **"Structural and microstructural changes in Zirconia in dilute chlorine atmosphere"**.

producido por **D. M. Pasquevich y F. Lovey**

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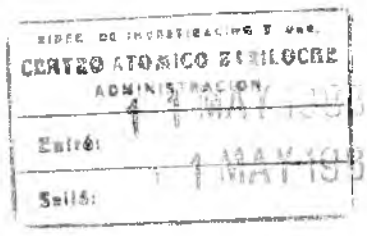

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De acuerdo a lo establecido en la Resolución de Presidencia N°1018, artículos 4° y 5°, se remite en devolución el presente expediente.

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producido por: D. M. Pasquevich y F. Lovey.

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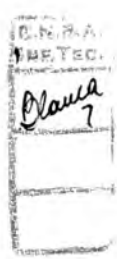

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