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PREPARATION OF SMALL α-IRON PARTICLES FROM AN AMORPHOUS $Fe_{91}Zr_9$ ALLOY

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Small α-iron particles with diameter less than 10 nm and enlarged lattice constant have been obtained by low temperature oxidation and reduction of an amorphous $Fe_{91}Zr_9$ alloy. *In-situ* X-ray diffraction has been used to study the transformation of the alloy at 300 °C which is far below the crystallization temperature. Scanning electron microscopy showed that the reacted sample consisted mainly of aggregates of small iron particles. This might offer a promising method for the effective preparation of heterogeneous catalysts.

1. Introduction

In the last few years metallic glasses have attracted attention as heterogeneous catalysts. The primary use has not been as catalysts in the amorphous state but rather as precursors for supported catalysts with new properties [1]. The metastable amorphous state represents a unique system for various solid state transformations [2]. In this letter we report the formation of small α-iron particles with enlarged lattice constant prepared from an amorphous $Fe_{91}Zr_9$ precursor by an oxidation/reduction treatment.

2. Experimental, results and discussion

A piece of a 10 mm wide amorphous $Fe_{91}Zr_9$ ribbon, which was produced by the conventional melt-spinning technique, was used for *in-situ* X-ray diffraction (XRD) measurements. A Siemens D500 equipped with a Paar high temperature cell was used to study the solid state reaction of the amorphous alloy *in-situ* using a reactive gas atmosphere. The diffraction patterns were recorded using Cu K_α-radiation and a defracted beam graphite monochromator. Images of the samples were obtained with a Phillips 515 Scanning electron microscope (SEM) using secondary electrons. The SEM is equipped with an X-ray energy dispersive spectrometer for chemical analysis.

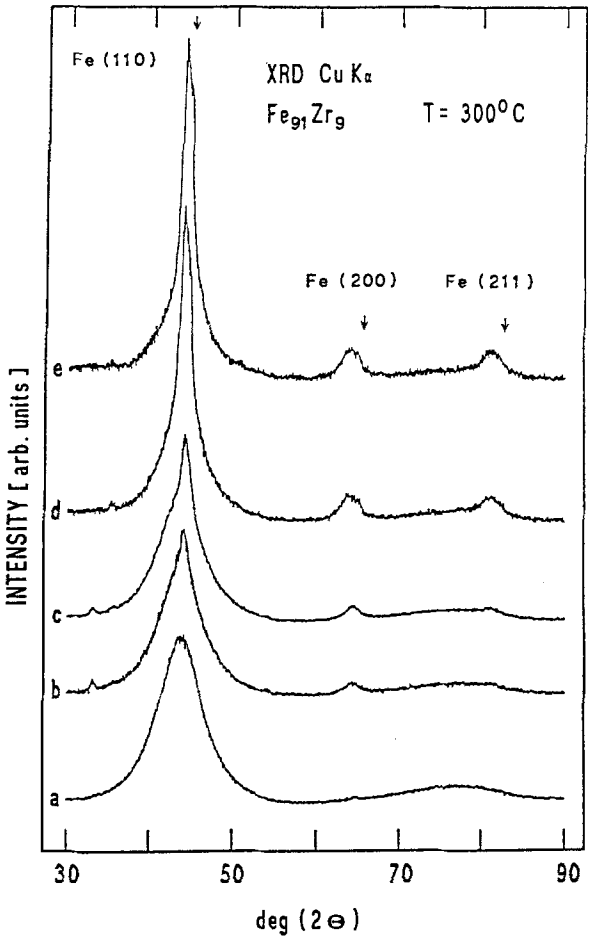

Fig. 1. *In-situ* X-ray diffraction spectra of amorphous $Fe_{91}Zr_9$ after various exposure times in oxygen and subsequent hydrogen atmosphere at 300 °C: a) as received, b) 69 h 0.9 bar O_2, c) 320 h 0.9 bar O_2, d) +76 h 0.8 bar H_2, e) +150 h 0.8 bar H_2. Peak positions for bulk α-iron are indicated by arrows.

Oxidation of the sample was done in an atmosphere of 0.9 bar pure oxygen for 320 h, the subsequent reduction in a hydrogen atmosphere of 0.8 bar pure hydrogen for further 150 h. The temperature for both treatments was kept constant at 300 °C which is well below the crystallization temperature of 600 °C determined by thermal analysis [3] in order to study the intrinsic properties of the amorphous state. Figure 1 shows the evolution of the structure of the $Fe_{91}Zr_9$ alloy as a function of the exposure to oxygen and hydrogen as seen by *in-situ* XRD. At about 34 deg 2Θ a weak reflection can be detected after 69 h. We attribute this reflection to a zirconium oxide [4], which is frequently formed upon oxidation of amorphous Zr-alloys [5]. The other broad features at 43.94 deg and

Table 1
Mean diameter and lattice constants of small α-iron particles from the observed (*hkl*) reflections

Miller-index (*hkl*)	Mean diameter (nm)	Lattice constant (nm)
110	9.2	0.2912 (5)
200	3.7	0.2914 (5)
211	4.3	0.2903 (5)

α-iron ($T = 20\,^{\circ}$C): 0.2866.

63.85 deg are due to α-iron. A small increase of the intensity of the α-iron (110)-reflection, which amounts 10% ± 2% is found from 69 h oxidation time to 320 h oxidation time (cf. fig. 1 curves b and c). No significant further growth is seen after 320 h in 0.9 bar oxygen at 300 °C. It is important to emphasize that no iron-oxide can be detected by means of XRD. We estimate the detection limit for a well crystalline compound under our experimental conditions to be 5%.

Changing the reaction gas from oxygen to hydrogen leads to an enhanced growth of the α-iron reflections. After further 150 h in 0.8 bar hydrogen at 300 °C the solid state reaction has reached a state in which the amorphous $Fe_{91}Zr_9$ alloy has partially transformed into a α-iron and a small amount of ZrO_2. Detailed analysis of the XRD reflections reveals very interesting properties of the formed α-iron.

Table 1 shows the average particle size, which has been calculated after correction for instrumental broadening and using the Scherrer equation, as well as the lattice constant for three different directions in space determined from the corresponding reflections. As can be seen very small α-iron particles are formed from the amorphous alloy by the treatment described above. In addition these particles feature an enlarged lattice constant which for bulk iron is only reached by thermal expansion at high temperatures in the so-called δ-phase.

Figure 2 shows an image of the transformed sample after the oxygen/hydrogen treatment obtained with an scanning electron microscope (SEM). The cross-sectional view shows aggregates of small spherical particles, which have been determined to consist of iron by means of energy dispersive spectrometry. Due to the limited resolution particles with the size as expected from XRD can not be seen.

The formation of small iron particles from an amorphous $Fe_{91}Zr_9$ alloy can be understood considering the metastability of the amorphous state as well as the large difference in enthalpies of oxide formation between iron and zirconium. By the first step i.e. oxidation of the alloy zirconium oxide will predominantly be formed [6]. An explanation can be given in terms of differing enthalpies of formation of the corresponding oxides which are −196.5 kcal/mol for Fe_2O_3 and −258.2 kcal/mol for ZrO_2 respectively [7]. The preferred oxidation of Zr leads to

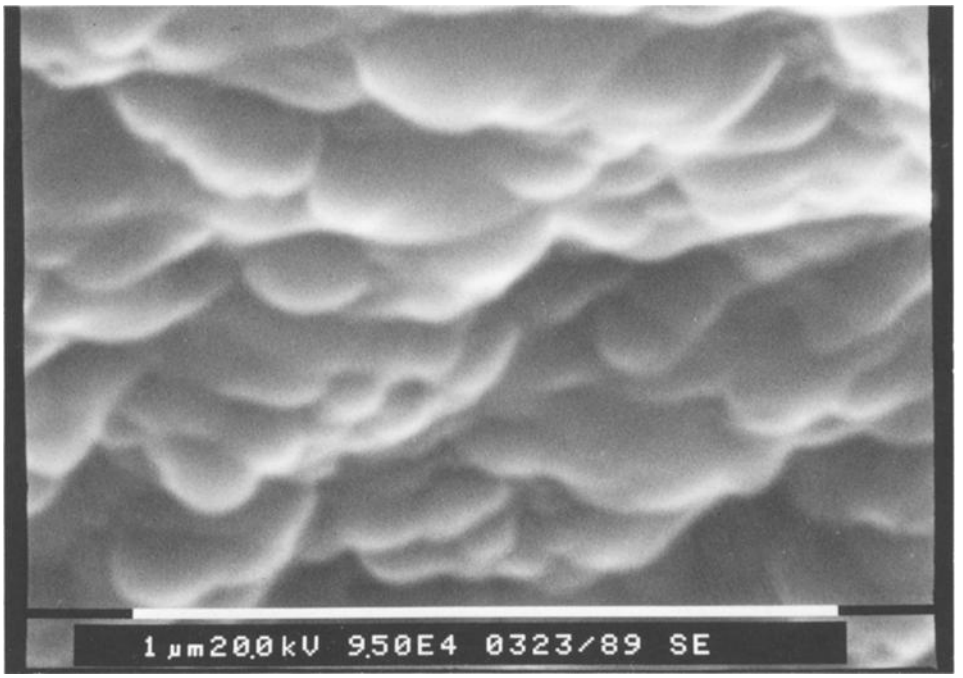

Fig. 2. Scanning electron micrograph of the cross section of the amorphous $Fe_{91}Zr_9$ alloy after oxygen/hydrogen treatment as explained in the text. The spherical particles consist of iron. The length of the white bar is 1 µm.

destabilisation of the amorphous alloy which can be produced by melt-spinning only for Zr concentrations from approximately 7 at.% to 12 at.% [3]. Thus the alloy will crystallize far below the nominal crystallization temperature and form the α-iron particles we observed. Further treatment of the sample with hydrogen enhances this process, possibly by formation of cracks, which facilitate diffusion of oxygen into the bulk. We propose that even in a reducing atmosphere the solid state reaction is triggered by the oxygen impurities, also present in pure gases as we used, which are sufficient to achieve further oxidation of the alloy. Selective oxidation of Zr in an 75% H_2/N_2 mixture has been reported by Armbruster et al. [8]. The reason for significant enlargement of the lattice constant of the formed particles is not obvious. One might suggest that crystallization of the alloy leads to high internal stresses which could cause a lattice enlargement. An alternative explanation could be that Zr atoms or Zr-O-complexes are built in the α-iron matrix and thus cause an expansion of the lattice. For obvious reasons there is a big interest in catalysis in aggregates of small metal particles with enlarged lattice constant since in some cases dependence of the reactivity of the particle size as well as of the lattice parameter has been found [9,10]. Test reactions with the described samples as well as detailed structural analysis of the formed iron particles are under way.

3. Conclusions

Low temperature oxidation of an amorphous $Fe_{91}Zr_9$ alloy far below the crystallization temperature results in formation of Zr-oxide and α-iron particles with unique properties. Amorphous alloys exhibit promising systems for such solid state reactions due to their thermodynamic metastability. This method may offer an effective way of catalyst preparation.

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