

Short communication

Formation of zirconium and nickel oxide nanoparticles via oxidation of quenched melted Ni–Zr alloys

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Abstract

Melted Ni₆₀Zr₄₀ alloy, synthesized via arc melting, was quenched in liquid nitrogen and subsequently oxidized at 1073 K for 2 h. The amorphous phase, resulting from quenching, is characterized by large open porosity and consists of agglomerates of small particles. Preferential oxidation and segregation induce distinct NiO and ZrO₂ agglomerates, which are composed of nanograins. The near spherical NiO particles have a diameter in the range 10–50 nm. The process may provide an approach for synthesizing composite oxide ceramic powders.

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1. Introduction

Quenching melted alloys induces the formation of amorphous phases, which can serve as precursors of nanostructured materials [1] and of oxide supported metal catalysts [2,3]. Amorphous Ni–Zr alloys have been studied in connection with their catalytic activities and, for this purpose, a comprehensive understanding of the changes occurring during their oxidation appears as a relevant subject [2,3]. In particular, the oxidation kinetics and the formation of nanograined zirconia of various Ni–Zr alloys, processed by the melt-spinning method have been studied [3]. Preferential oxidation of Zr is anticipated, due to the stronger oxygen affinity of Zr, and has been indeed pointed out in similar [3,4] and other alloys [5,6]. Accordingly, one could take advantage of such preferential oxidation to find means for obtaining nanosized oxide particles through a top-down approach. The particular interest for NiO and ZrO₂ (as well as NiO–ZrO₂ composites) is motivated by

their attractiveness for applications such as, for instance, electrodes and catalysts [7].

The purpose of this study is to investigate the first steps of the possibility of such a top-down approach for synthesizing NiO–ZrO₂ composite nanosized powders via oxidation of quenched Ni–Zr. Incidentally, this work may also provide information that might shed some more light on properties of amorphous Ni–Zr alloys that could be relevant to their application as catalyst or precursor of catalysts. To this end, we study the Zr₄₀Ni₆₀ (60 at % Ni) alloy, prepared by arc melting and subsequently quenching in liquid nitrogen.

2. Experiments

The experimental set up is shown in Fig. 1. The Zr–Ni alloy of pure elements (purities of 99.95% and 99.99% for Zr and Ni, respectively) of 15.0 g was prepared by arc melting, under ultrahigh purity helium atmosphere. The alloy ingot was re-melted four times to ensure good homogeneity. Then, quenching was performed as illustrated in Fig. 1. Prior to quenching in liquid nitrogen, the sample was removed from its copper mold (water

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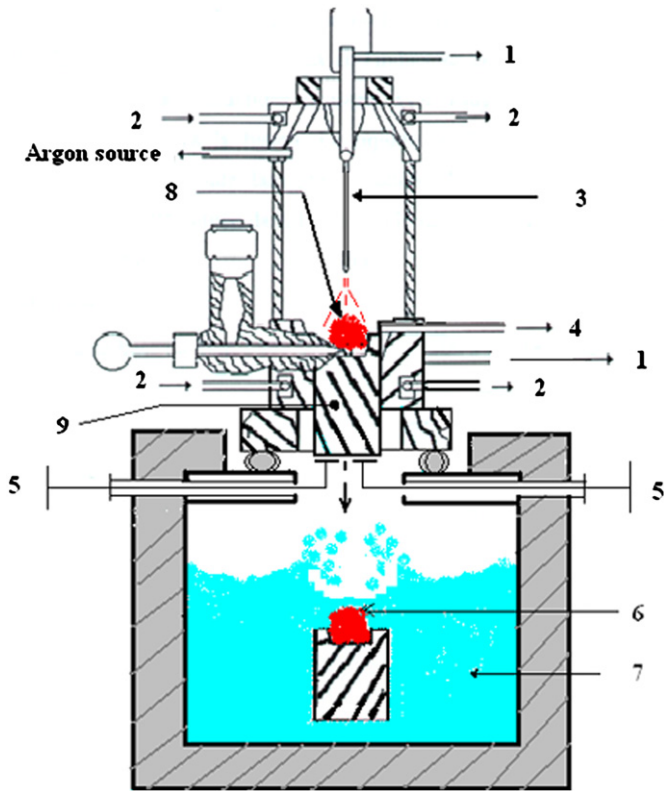


Fig. 1. Experimental set-up illustrating alloy preparation and quenching in liquid nitrogen: 1, generator (+, -); 2, into the cooler; 3, electrode (W); 4, vacuum frame; 5, trap; 6, sample quenched in liquid nitrogen; 7, liquid nitrogen vat; 8, sample in fusion; 9, crucible.

cooled). This step took about 20–30 s during which some nucleation processes may have been developed. During this time, the sample remained red corresponding to a temperature close to 1250 K. The oxidation process under oxygen atmosphere and isothermal conditions (2 h at 1073 K) was recorded using a Setaram TG-DTA 92-1600 microthermalance. Characterizations were made by scanning electron microscopy (SEM) (Philips environmental: FEI/Philips XL30 FEG ESEM) coupled with an energy dispersion spectroscopy analyzer (EDS) and a differential thermal analyzer (DTA).

3. Results and discussion

3.1. Quenched material

The SEM images of quenched samples, of the chemically etched areas after mechanical polishing, show the presence of dendritic phases (Fig. 2), also observed in rapidly solidified Co–Sb alloys [8]. At this stage, quenching in liquid nitrogen gives rise to an important open porosity. This, in turn, considerably enhances the segregation effects and preferential oxidation reported elsewhere [3–6]. Apparently, in these works, the amorphous alloys were free from discernible open porosities, which could be due to the quenching process. Fig. 3 shows that the as quenched alloy exhibits a form of skeleton composed of particles with diameter of about 170 nm, which are clearly noticeable at the triple point (Fig. 3a). In Fig. 3, the

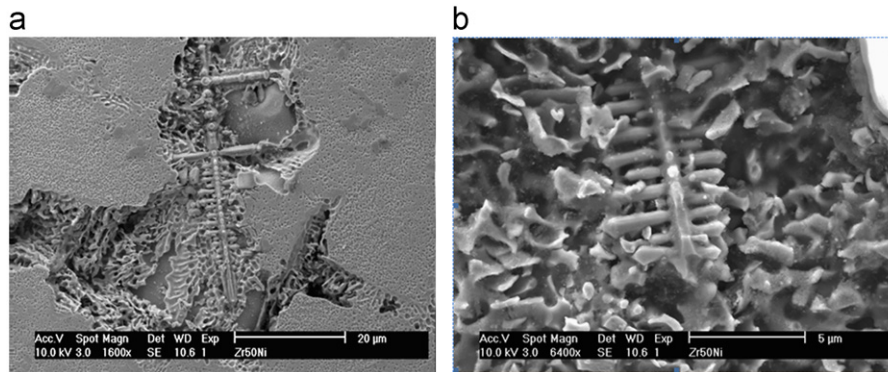


Fig. 2. SEM observations of chemically etched area of a $Zr_{40}Ni_{60}$ alloy for two magnifications. Some dendrite phases appear and a large porosity is revealed.

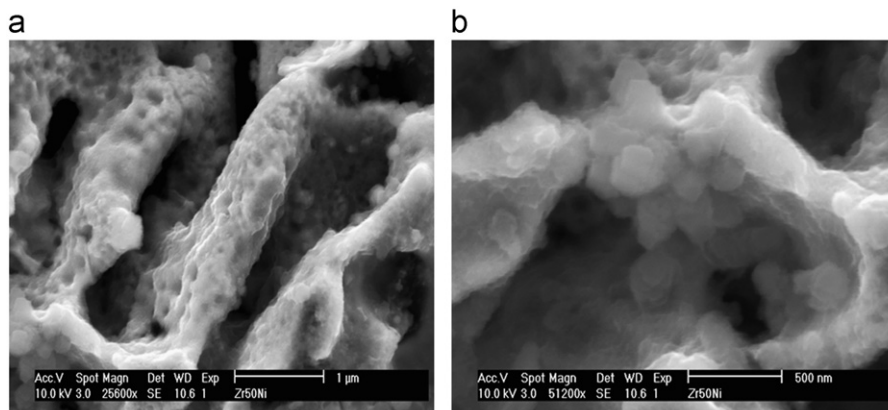


Fig. 3. SEM observation of an area of quenched $Ni_{60}Zr_{40}$ alloy with two magnifications. The porosity (more likely open) is large. The quenched material seems to be composed of fine grains (with sizes of about 170 nm).

porosity is estimated at nearly 50%. This relatively large open porosity, which can be attributed to the quenching method, will make oxidation homogeneous and enhance its kinetics.

The DTA results (Fig. 4), in heating mode at a rate of 5 K/min, reveal two endothermic peaks near 1350 K and 1393 K, which, as expected reflect the dominance of the amorphous state. The ratio of the enthalpies corresponding to the two phases is close to 3 in favor of the first one.

Typical EDS analyses, performed on quenched alloys, are shown in Fig. 5a, where no discernible contamination during the quenching process is observed.

3.2. Oxidized material

Oxidation at 1073 K of the quenched alloy produces a very brittle substance (having a green aspect). Samples, obtained after a rough milling, are shown in Fig. 6. The pronounced

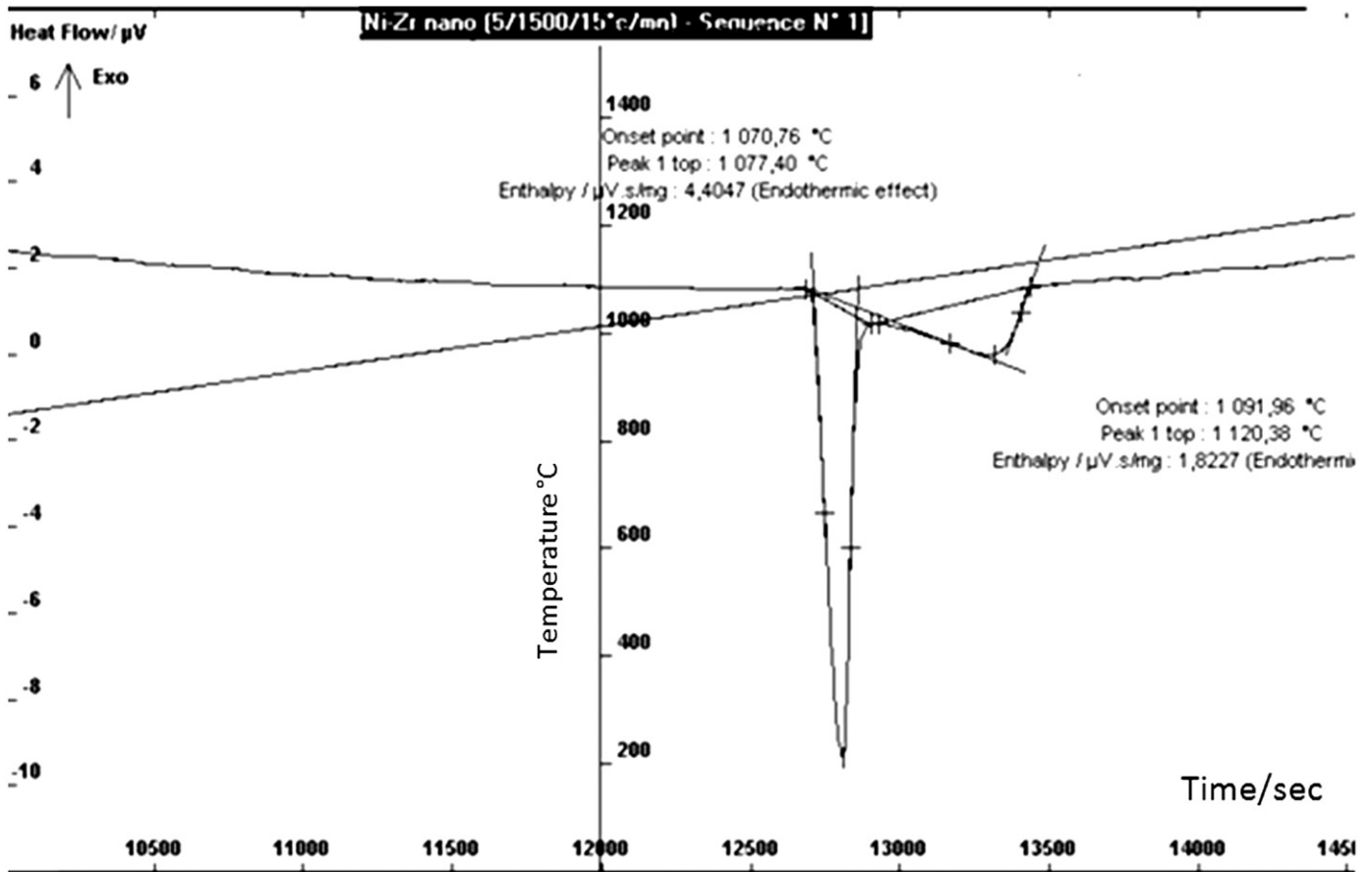


Fig. 4. DTA curves of Ni₆₀Zr₄₀ quenched alloy with a heating rate of 5 K/min. Two endothermic peaks, characterizing the amorphous state of the quenched material, emerge (at the top peaks located at 1350 and 1393 K).

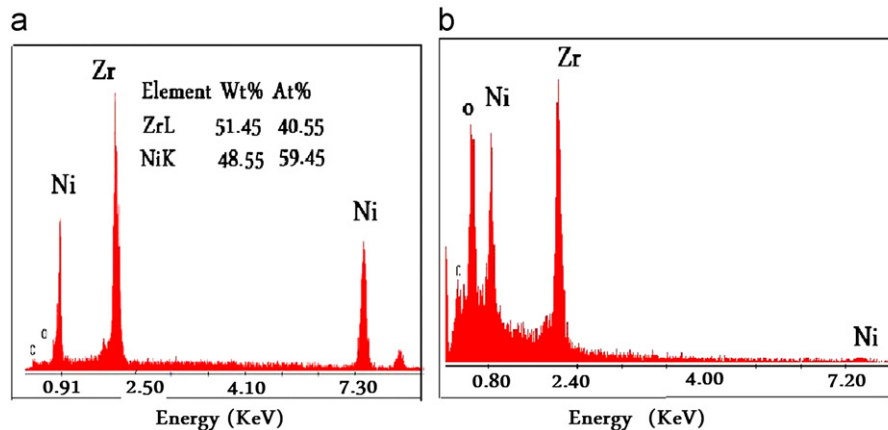


Fig. 5. EDS spectra of Ni₆₀Zr₄₀ alloy: (a) alloy quenched in liquid nitrogen and (b) the same alloy after oxidation at 1073 K under oxygen atmosphere for 2 h.

brittleness of this product is a characteristic of its oxide ceramic's nature. This is, to a certain degree, corroborated by EDS analysis of Fig. 5b, which indicates the possible formation of oxides. A white contrast and a stratified morphology emerge in Fig. 6, indicating some heterogeneous structure of the oxidized alloy. This observation, by itself, constitutes a strong evidence of segregation effects that are

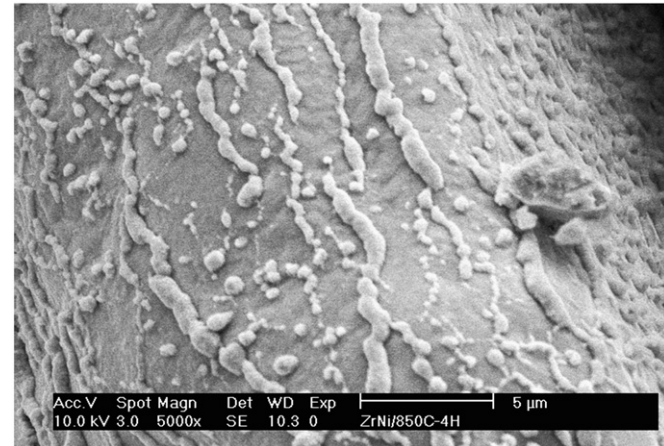


Fig. 6. Typical SEM micrograph of a fractured surface of quenched $Zr_{40}Ni_{60}$ alloy after oxidation under oxygen atmosphere during 2 h. The fractured surfaces were obtained by rough milling. The microstructure, white worms over a dark background, reflects Ni segregation (cf. Fig. 7).

induced by the oxidation process. This is furthermore confirmed as shown in Fig. 7, where EDS analyses in white and dark agglomerates are performed indicating Ni and Zr rich regions. A quasi-complete oxidation at 800 K (in air for 1 h) of Zr in amorphous $Zr_{36}Ni_{64}$ in the form of a 20 μm thick ribbon has been pointed out [4]. Accordingly, given the substantial open porosity (Fig. 3) of our as quenched samples along with the higher oxidation temperature (1073 K), the same conclusion can be anticipated.

The agglomerates of nickel rich zones are composed of well distinct nanoparticles whose diameter can be estimated to be in the range 10–50 nm (Fig. 7). Although not clearly perceptible, the dark background of Fig. 7 is more likely constituted of smaller ZrO_2 nanoparticles as reported elsewhere [2]. We are aware that the confirmation of the nature of the nickel rich agglomerates (i.e., oxidation extent and the presence of metallic Ni nanograins) requires further characterizations, which are beyond the scope of this paper. However, there are strong indications that these agglomerates are very likely composed of crystalline NiO nanoparticles [9]. In this reference, crystalline nanoparticles, with sizes ranging from 20 to 60 nm, were indeed obtained by oxidation of amorphous Ni nanoscale powders at 1173 K. In our case, since the oxidation of Zr precedes that of Ni in the alloy (which, as mentioned above, consists of fine amorphous particles with dimensions near 170 nm), almost similar conditions are achieved. The other observation that can be drawn from Fig. 7 is the

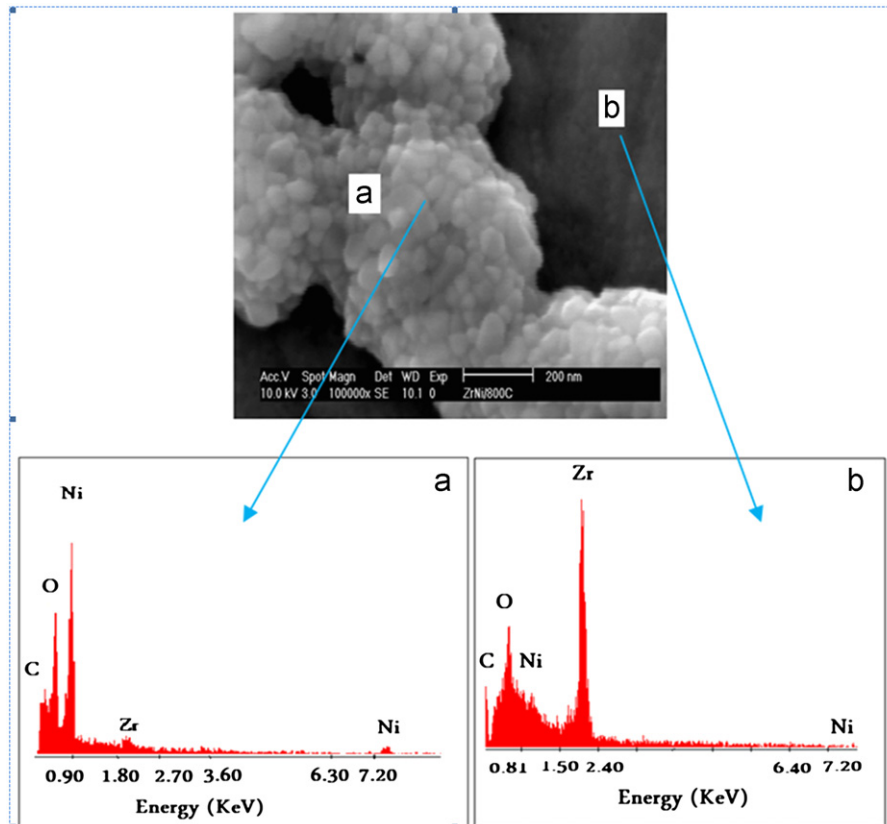


Fig. 7. SEM micrograph and EDS spectra of two zones of quenched $Ni_{60}Zr_{40}$ alloy after oxidation under oxygen atmosphere for 2 h: (a) nickel oxide zone and (b) zirconium oxide zone. The segregation of NiO and ZrO_2 nanoparticles appears conspicuous. The sizes of NiO are in the range 10–50 nm.

unambiguous display of the segregation effects, which arises from the different affinities of the alloying elements to oxygen. These two microstructural features can be considered as contributions of this work, which could bring further insight to the properties of these materials relevant to the catalysts or precursors of catalysts applications.

The composite NiO–ZrO₂ that is obtained via oxidation of quenched Ni–Zr alloy can be easily milled, as it is very brittle, to give a homogeneous mixture of NiO and ZrO₂ agglomerates of nanoparticles. The choice of appropriate sintering techniques and conditions could give means for controlling properties such as inter or intra-agglomerates porosities. Hence, the results of this work could provide a framework for synthesizing composite powders alternative to, for instance, the spray drying method [7].

4. Conclusion

This work shows strong evidence that oxidation of quenched Ni₆₀Zr₄₀ alloy at 1073 K in an oxygen atmosphere produces distinctly large NiO and ZrO₂ agglomerates composed of nanograins with dimensions less than 50 nm. The formation of such agglomerates can be traced to segregations effects due to the preferential oxidation of zirconium. These inferences may provide motivations for further investigations aimed at the prospect of a top-down approach for synthesizing composite oxide ceramic nanosized powders.

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