

Role of oxygen and nitrogen in mechanical alloying mechanism of Ni–Ti powder mixtures

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In this study, the critical milling behaviour of Ni–Ti powder mixtures was evaluated in relation to the effect of atmospheric gases, more specifically to oxygen and nitrogen. Within the experimental conditions used, it is shown that both gases play an important role in the alloying process and that not only oxygen gas reacts with the mechanically alloyed powders but also nitrogen. The most effective mixing occurred for the mixtures with the highest contaminant contents.

Keywords: NiTi, Mechanical alloying, Critical milling behaviour, Powder processing, Shape memory alloys

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Introduction

It is known that the properties of NiTi shape memory alloys depend strongly on the exact chemical composition, processing history and impurity level.^{1,2} Contaminants such as oxygen and nitrogen can dramatically affect the properties of the NiTi shape memory alloy, and in high quality bulk materials, the levels of those impurities should be kept below 1000 and 50 ppm respectively.³ The pick-up of those gases occurs basically during the processing of the alloys. Therefore, special attention should be given to that type of contamination on this stage.

Mechanical alloying (MA) is a powder metallurgy processing technique that has been used to synthesise both equilibrium and metastable phases of commercially useful and scientifically interesting materials.⁴ As has been pointed out frequently, the technique of MA was developed out of an industrial necessity in the 1960s by J. Benjamin to produce oxide dispersion strengthening nickel-based superalloys.⁵ Since the late 1980s, a considerable number of investigations have been devoted to the processing of NiTi alloys by MA, starting from mixtures of elemental powders.^{6–9} Overall, the technique of MA involves repeated cold welding, fracturing and rewelding of the powder particles due to the highly energetic collisions with the grinding media in a high-energy ball mill.⁶ During MA, a proper balance should be reached between the processes of welding and fracturing. Usually, when powder particles of ductile metals are milled, this balance is controlled mostly by the addition of an organic surfactant known as a process control agent (PCA). However, when a reactive metal like titanium is being milled, the levels of contaminations introduced in the material during milling (either by the grinding medium or by the milling atmosphere) are, in many cases, high and unacceptable.⁴ It is known that

careful milling practice can reduce the overall level of contamination to well within acceptable limits. However, relatively little attention has been paid to the effects that different levels of contamination (mainly the one arising from the oxygen and the nitrogen from the lab's atmosphere) might cause in the MA process evolution of Ti–Ni powder mixtures and, in particular, to what is called the 'critical milling behaviour' (CMB). The CMB is related with the sticking to the milling media due to the ductile behaviour of the Ti–Ni powders.¹⁰ As a first consequence, a large amount of powder is pasted onto the inner surface of the vial and will be stored in layers where no further processing can take place. The second consequence is a significant change of the component concentration of the remaining powder that is being processed. At the end of the MA process, a low powder yield will be obtained. Therefore, the remaining question is: 'Is the CMB dependent on the level of oxygen and nitrogen present in the milling atmosphere?' This is a relevant and quite timely question since, in open literature, few publications refer to the powder yield achieved with the MA of Ti–Ni powders.^{10,11}

Experimental

To solve this issue, several MA experiments were conducted in a planetary PM100 mill (Retsch) using mixtures of pure elemental Ti (Alfa Aesar, 99.9%, <105 µm, spherical shape) and Ni (Acros Organics, 99.9%, <44 µm, irregular shape) powders in the stoichiometric ratio of 50 at-%Ni. X40Cr13 stainless steel vials (250 mL) and balls (10 mm) were used while each powder charge was 20 g and the charge of balls amounted to 200 g (ball/powder weight ratio of 10:1). The milling speed ranged between 150 and 300 rev min⁻¹, and the duration of MA went up to a maximum of 32 h. To avoid temperature increase during MA, milling periods of 10 min were alternated with 5 min periods of rest. In specific milling times (1, 2, 4, 8, 12, 16, 20 and 32 h), the powder yield was estimated by the ratio between the weight of the remaining powder and the weight of the initial amount of powders. Subsequently, a small amount of the mixed powder was

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