Mechanism of reaction of molten NiTi with EBM graphite crucible

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Ultra clean NiTi shape memory alloy was produced by electron beam melting of Ni rich vacuum inductionally melted butts together with pure Ti chunks in both condensed and electrographite crucibles. A hollow cathode discharge gun was used for heating up to 1623, 1653 and 1693 K and holding the charge materials under vacuum for 300, 600, 900 and 1200 s. Effects of temperature, time and compactness of the crucible on formation/disappearance of the hard compounds like Ni_3Ti, Ti_4Ni_2O, Ti_4Ni_2C, Ti_3Ni_2OC and TiC were determined by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. A combination of the experimental results with the kinetic rate equations indicated that the reaction between NiTi and the crucible obeyed first order transfer kinetics with carbon intake activation energy of 225·8 kJ mol^{-1} for the NiTi shape memory alloy melt.

Keywords: NiTi, EBM, SMA, Transfer kinetics, Mechanism, Graphite crucible, Condensed graphite, Electrographite

Introduction

The NiTi intermetallic compound displays shape memory effect, super elasticity, two way shape memory characteristics and all round shape memory effect together with biocompatibility, corrosion resistance, damping power, close to bone strength, water resistance, superior fatigue life and high specific electric resistance.[1–7] These properties make NiTi an attractive biomaterial usable in smart devices of both medical and engineering applications. Cardiovascular incision, orthopedic surgery, orthodontia, surgical implants and separation systems of satellites are a few examples.[7–11] During past two decades, extensive work has especially been carried out on NiTi alloys to produce NiTi shape memory alloys (SMAs) by powder metallurgy, self-propagation high temperature synthesis,[4–7,11–13] vacuum induction melting (VIM) and vacuum arc melting processes.[14–19] Vacuum melting technology has, in the past, almost exclusively been used for NiTi alloys commercial mass production.

Less attention has, however, been paid to the electron beam melting (EBM)[20–25] as an alternative way for production of NiTi SMAs and other Ti containing alloys. Since 1950, EBM has continuously been developed for fusing of high melting point metals.[26–28] This method is widely used even to an industrial scale for melting and/or remelting of the Ti alloys. A method is recently proposed to achieve a low carbon concentration during EBM processing of NiTi SMAs using the water cooled copper crucibles.[20–23] The electron beam melting/casting technique is now accepted as a novel method for production of the Ti alloys.[20–23,27,28] Desirable memory effects can, in general, be obtained with 49–50·7 at.-%Ti in the alloy. Binary alloys containing less than 49·4 at.-%Ti are, for example, extremely hard and brittle and cannot easily bear deformation processing to reach the eventual geometric shape.[29–32] The binary Ti–Ni phase diagram[3] (Fig. 1) demonstrates that deviation from stoichiometric concentration causes a considerable precipitation of brittle intermetallics in the NiTi matrix.[3] Figure 2 represents the binary Ni–C and Ti–C systems and the isothermal section of the ternary Ni–Ti–C system at 1500 K.[14] Formation of Ti_2Ni, Ti_2Ni_3, $TiNi_3$, Ti_4Ni_2 and Ti(N,C,O) compounds affects on the workability, ductility, strength, hardness and phase transformation temperatures of the material and its functional properties.[30–35] Absorption of oxygen and nitrogen during heating, melting and annealing can also dramatically influence the mechanical properties and workability of TiNi samples.[34]

The EBM can decrease concentrations of the impurity elements such as N, O and H through their out-gassing. The decomposition of Ti_4Ni_2O and release of oxygen can partially occur during the electron beam remelting process.[20,21,23–25] The EBM can, therefore, be assistive in remelting of the NiTi ingot butts produced even by other methods like VIM, helping to produce more workable TiNi SMA.

During both melting and remelting, NiTi tends to react not only with oxygen but also with the crucible and mould surfaces. Zhang *et al.*[19] applied an alternative VIM method for investigation of the reaction between the NiTi melt and the graphite crucible. The activation energy they obtained for TiC formation in VIM was 247 ± 34 kJ mol^{-1}. Otubo *et al.*[20] showed that the carbon contamination of the NiTi produced by EBM in a water cooled crucible was 4 to 10 times lower than that of the

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