Characterization of Complex Phase Transformations in Aluminum Doped Ni – Ni₃B Eutectic Alloy

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Abstract: The binary Ni – Ni₃B eutectic alloy doped with small additions of aluminum has been studied by Differential Thermal Analysis (DTA), Energy Dispersive X – ray Analysis (EDXA), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Some complex phase transformations were observed in form of precipitations which are probably responsible for the high hardness values of the alloys. The thermal response of this hard alloy in DTA during slow cooling showed the existence of this complex phase. From X-ray diffraction experiments and energy dispersive X – ray analysis (EDXA), a chemical composition of Ni₃AlBₓ was proposed for the ternary complex phase. The lattice parameter of this phase varies between 10.49 Å and 10.55 Å. It was also reported that no mutual crystallographic orientation relationship could be observed between Ni (α) and Ni₃B in the Ni – Ni₃B eutectic in the presence of aluminum.

Key words: alloy, solidification, precipitation, microstructure, crystallography, eutectic, addition

INTRODUCTION

One of the major problems facing most of our industries is the problem of wear and corrosion. Most industries spend a lot of their resources to combat this problem. To arrest this situation, a family of Nickel hard alloys were developed called “Hardfacing Alloys”[1,2,4,5,6]. They are made up of a metallic matrix (Nickel) and hard phases such as carbides, borides and silicides whose nature depend essentially on the type of metallic additions (chromium, molybdenum, tungsten, titanium, vanadium and aluminum) and non metallic additions such as carbon, boron and silicon. The carbides, silicides and borides distributed in the Nickel solid solution are the main source of their wear resistance while chromium addition enhances their corrosion resistant property[7]. It has been reported that their wear resistance and high-temperature compression strength are significantly enhanced by the formation of boride[8]. It has also been reported that boron decreases the melting point of Nickel and gives the alloy self-fluxing properties which are useful for powder welding[1,3]. These alloys are applied by several spraying and deposition techniques[9]. The binary eutectic Ni – Ni₃B is a very dominant feature of these alloys. This eutectic composition is Ni – 16.2at%[10].

It has been observed that the effect of various elements such as titanium and vanadium on the Ni – Ni₃B has been reported[11,12] but the influence of aluminum on this dominant binary eutectic Ni – Ni₃B in these alloys has not been particularly studied. This has informed the present work to investigate the influence of aluminum on the thermal, crystallographic and microstructural behaviours of this eutectic under slow cooling in DTA.

MATERIALS AND METHODS

Sample Preparation: To the eutectic composition Ni - Ni₃B were added pure aluminum element (0.5 to 1at%). Accurately weighed components of each alloy were arc-melted in an argon atmosphere using non-consumable tungsten electrode. This operation was repeated two or three times to ensure the homogenization of these samples. The melting behaviour and the phase formation were determined by differential thermal analyzer (DTA) model DTA 404PC in our laboratory. This apparatus allows the automatic control of thermal programmes and automatic analysis of the results. The heating and cooling rate is 5°C min⁻¹.

Characterization of the Alloys: The microstructure of the samples was examined using optical microscopy and scanning electron microscopy (SEM-JSM35) equipped with energy dispersive X-ray analysis.
The nature of the phases present in these samples was examined by X-ray diffraction. More accurate characterizations were obtained by transmission electron microscopy (TEM) and electron diffraction performed on thin foils in a JEM – 200CX. Thin foils were obtained by electropolish in an electrolyte containing 24.257% HSO₄ in H₂O at room temperature under 10V.

RESULTS AND DISCUSSION

The thermal response of this alloy is shown on the DTA thermogramme in Figure 1 while Figure 2a depicts the isothermal projection of the Ni-B-Al system at 800°C. As mentioned above the heating and cooling rate is 5°C min⁻¹. It should be noted that in the ternary alloy Ni-B-Al containing 1%Al quenched from the liquidus at an estimated cooling rate of 10⁴°C/s, the microstructure is simple with the scanning electron microscopy revealing a primary dendritic phase of Ni (α) surrounded by a lamellar eutectic Ni – Ni₃B. However after slow cooling in DTA at a cooling rate of 5°C/min, the microstructure is complex. This is probably due to solid state transformation occurring at low temperature during slow cooling and large undercooling in the alloy. From the DTA thermogramme, the peak at 1239.6°C shows the crystallization of the primary phase of Ni (α). The SEM observations show that this primary phase is composed of dendrites of Ni (α) (Figure 2b).

The solidification of this alloy progressed by the appearance of another peak at 1105.3°C. This peak corresponds to the formation of a solid state precipitate – like structure between Ni (α) and a ternary phase τ as shown in the SEM micrograph of Figure 2b. Figure 2c shows the electron diffraction pattern of this ternary phase τ as well as the diffraction index in Figure 2d. As the cooling continued, the final peak observed at 1098.7°C on the DTA thermogramme could only be associated with the formation of some pockets of the lamellar eutectic Ni (α) – Ni₃B in some interdendritic spacings as depicted by the SEM micrograph of Figure 2b. From XRD experiments the structure of this complex ternary phase τ is cubic of the type M₃C₆ observed in the ternary systems Ni - B - Ti[11] and Ni-B-V[12]. From the Energy Dispersive X-ray Analysis performed on this alloy, the chemical composition of Ni₂Al,B₆ could be proposed for this τ phase. This is similar to that reported by Stadelmaier and Fraker[13]. In fact recent studies of the Ni-B-Al system by Boettinger and Campbell[14] reported that simulations quantitatively predicted the observed precipitation of the intermetallic ternary τ phase. The lattice parameter of this phase varies between 10.49Å and 10.55Å. The domain of existence of this phase has been proposed by Stadelmaier and Fraker[13] as shown in Figure 2a. It could be observed from the TEM micrograph of Figures 2c and d that this ternary phase is in perfect coherence with the Nickel phase. This could be explained by the fact that the two phases are face centered cubic with the lattice parameter of the τ phase about three times that of Nickel (a = 3.56Å) hence the atoms of the ternary τ phase could easily
Fig. 2: (a) Ternary Ni - B - Al phase diagram showing the domain of existence of the τ phase (b) Scanning Electron Micrograph of the slowly cooled 1at% Al doped Ni - Ni3B eutectic (c) Electron diffraction pattern and (d) Diffraction index showing a perfect coherence between Ni (α) and τ phase.

substitute the regular atomic sites of Nickel. Furthermore some crystalline faults were observed in the primary phase Ni (α) which could not be clearly characterized.

The relation between the thermal effect due to the change of state and the surface area (S) of the peak in DTA experiment is given by:
Fig. 3: (a) Transmission Electron Micrograph showing the lamellar Ni - Ni₃B eutectic observed in the interdendritic spacings of the alloy (b) Electron diffraction pattern and (c) Diffraction index depicting the absence of mutual orientation relationship between Ni (α) and Ni₃B.

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S \approx \int_{T_1}^{T_2} \theta dT \approx \frac{mq}{K}
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where

- \( m \) = sample mass
- \( q \) = enthalpy change per unit mass
- \( K \) = heat transfer coefficient
- \( T_1 \) = Onset temperature
- \( T_2 \) = Final temperature of reaction
From our DTA experiments, the enthalpy of transformation for the alloy undergoing solid state transformation is estimated at 65.32 J/g. With the mass of the alloy being 50mg, the surface area of the peak during transition at 1105°C was estimated at 4x 10^-3 m^2. From the above relation and experimental data, the heat transfer coefficient (K) between the crucible and the melt has been estimated at about 8.2x 10^4 Wm^-2K^-1. The difference between this value and that obtained by Casanova et al. could probably be explained by the relative thickness of the crucible used in each experiment.

From crystallographic viewpoint, no mutual orientation relationship between Ni (α) and Ni,B was observed in the Ni – Ni,B binary eutectic as shown by the TEM micrograph, electron diffraction pattern and the diffraction index of Figure 3 whereas a perfect coherence was observed between the τ and Ni (α) phases (Figure 2). However in similar eutectic doped with vanadium, this mutual orientation relationship was prominent[13]. The influence of aluminum addition could be said to be responsible for the absence of this mutual orientation relationship due to the formation of a more prominent ternary τ phase.

**Conclusion:** Ni–Ni,B eutectic doped with aluminum has been investigated with various microscopic characterization techniques such as differential thermal analysis (DTA), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis, X-ray Diffraction and Transmission Electron microscopy (TEM).

Preliminary results of the phase changes due to the precipitation of the ternary τ phase and their crystallographic orientation relationships have been presented.

Perfect coherence between the ternary τ phase and Ni (α) was observed while mutual orientation relationship could be safely said to be absent between Ni(α) and Ni,B in the presence of aluminum.

**REFERENCES**