Original Article

Thermal and microstructural study of slowly cooled Ni-B hard alloys containing Ti

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ABSTRACT

Binary Ni-B alloys containing varied amounts of titanium were prepared and investigated in this study. Differential Thermal Analysis (DTA) was used to study the solidification and transformation behavior of the alloys, while Optical Microscope (OM) and Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray Analyzer (EDX) were used to study the microstructure of the alloys. Microscopic and thermal investigations of the alloys revealed the presence of two major primary phases Ni (α) and τ with other binary and ternary eutectic structures being present in the hard alloys. The addition of titanium to the Ni-B system enhanced the formation of the ternary phase τ, while solid-state eutectoid transformation of the τ phase was observed in alloys with low titanium composition. But such transformation was not detected in alloys with high titanium contents, which enhanced the formation of hard boride phases.

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1. Introduction

The gradual deterioration of metallic components in industrial plants occurs mainly due to corrosion and wear phenomenon [1]. A growing number of studies [1-8] on Ni-based superalloy in the past decade reveal the potential of increasing thermal and microstructural stability of this type of material by alloying with refractory elements such as Ti, Ta, V, Cr, etc. Corrosion and wear often add up to result into great damage in various industrial components [9]. In most applications of industrial components, the surfaces are subjected to strong mechanical forces and thermal cycle. In such situations, it is efficient and more economical to modify the surface properties rather than improving the bulk properties [7,10,11]. The surface properties such as wear, abrasion and corrosion can be successfully improved by methods like induction hardening, laser induction, carburizing, nitriding, and internal oxidation [12-16]. Nickel-based hard alloys have a unique combination of properties that makes them suitable for peculiar purpose applications mostly in petrochemicals, glass, nuclear, automobile, pharmaceutical, etc., industries to increase wear and hot corrosion resistance [5,17-20]. These hard-facing alloys contains several kinds of hard phases (carbides, borides,
silicides) and these hard phases depends on the various metallic and non-metallic elements used to ‘marry’ the base metal, nickel. While boron, silicon and carbon are used as non-metallic additives; titanium, vanadium, chromium, etc., are used as metallic additives [20]. The borides, carbides and silicides distributed in the nickel matrix are the major source of the wear, hot corrosion and abrasive resistance of the alloys.

It has been reported that titanium, vanadium, chromium, tungsten enhances the wear, hot corrosion, abrasion resistance; and increases the hardness, high temperature compressive strength of the coatings by formation of hard boride phases [21–24]. Also, studies have shown that boron depresses the melting temperature of the mixture and plays a critical role in self-fluxing properties of the alloy making it practical for powder welding [25]. In the study of influence of titanium addition on the microstructure and hardness properties of near-eutectic Al-Si alloys, Muzaffer and Erdem [26] reported an increase in hardness, mean area and coarsening of the alloy when titanium content is increased. Different morphologies such as flakes and petals were observed depending on the solidification conditions and temperature history of the alloys. Recently, Shakoor et al. [2] reported the synthesis and properties of electrodeposited Ni-B-Zn ternary alloy coatings. The result shows that the addition of zinc to Ni-B results in increase in roughness, improvement in crystallinity and nanomechanical properties. However, there are few reports on their microstructure and mechanical properties [2,21,26,27].

Owing to the importance of Ni-B superalloys in high technological application where they are subjected to extreme thermal loading and temperature cycles, a study of their microstructure and thermal properties is very vital. In this study, we investigate the evolution of the thermal properties and phase microstructure of slowly cooled Ni-B: Ti ternary hard alloys with different proportions of titanium content.

2. Materials and methods

Ni-B: Ti ternary alloys with varying composition of titanium (2–11 wt.%) were prepared from separate components of pure titanium and binary Ni-B alloy with composition as highlighted in Table 1. All the metal components are of 99.99% purity. The components were accurately weighed and subsequently melted in an electric furnace for alloying process. Differential thermal analyzer (Netzsch DTA 404 PC) at Center for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria was used to determine the solidification path and phase formation of the alloys in the heating and cooling regimes. The heating and cooling of the experimental samples were carried out at heating rate (HR) of 20 °C/min for low temperature regions (25–800 °C) and 10 °C/min for high temperature region (800–1350 °C). The liquidus projection of the Ni-B:Ti ternary system according to Schobel and Stadelmaier [28] is shown in Fig. 1 with the positions of the alloys indicated as A, B, C, D and E. Metallographic observations of the alloys have been made by optical microscopy and Scanning Electron Microscope (SEM) equipped with energy dispersive X-ray analysis system. Before microstructural analysis, sample surface was etched with an etchant consisting of 5g FeCl3 with 10ml HCl dissolved in 50ml H2O for Optical Microscope and SEM observations.

3. Results and discussion

3.1. Thermal properties

Thermograms for the alloys are shown in Fig. 2(a)–(e). For alloy A containing 2 wt.% Ti and 5 wt.% B in 93 wt.% Ni, an endothermic effect is shown at 1081.2 °C and a prominent exothermic reaction is shown at 1306.9 °C during heating. The endothermic effect corresponds to melting reaction of the alloy, while the exothermic effect corresponds to changes in phases, and recrystallization. During slow cooling in the thermal analyzer, exothermic effects were exhibited during solidification at 941.4 °C and 881.6 °C. The exothermic effects shown during cooling for alloy A appeared more like an eutectic transformation after solidification if we consider the shape of the peaks. In the same vein, the DTA spectra for alloy B (85Ni12B3Ti) is presented in Fig. 2(b). Expectedly, two endothermic reactions were observed during heating to precede the main peak corresponding to the melting phase transformation at 982.1 °C, 1026.3 °C, and 1121.5 °C respectively. The two preceding low peaks can be attributed to initial phase transformation processes before the appearance of the major reactions at 1121.5 °C and 1342.5 °C. During cooling process, two successive broad exothermic peaks corresponding to phase reactions at solidification onset (1304.7 °C and 1167.1 °C) and a sharp exothermic effect at 978.0 °C corresponding to eutectic transformation were observed.

As shown in Fig. 2(c), thermal characteristic of alloy C with composition 86Ni6B8Ti can be likened to that of alloy A, mainly during heating process with a prominent exothermic reaction at 1094.7 °C which shows the major transformation or recrystallization effect and followed by a low exothermic peaks at 1297.9 °C situated at the edge of heating cycle.

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**Table 1 – Chemical compositions of the prepared alloys.**

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Compositions (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>A</td>
<td>93</td>
</tr>
<tr>
<td>B</td>
<td>85</td>
</tr>
<tr>
<td>C</td>
<td>86</td>
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<tr>
<td>D</td>
<td>80</td>
</tr>
<tr>
<td>E</td>
<td>82</td>
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</table>
However, during cooling cycle, no observable transformation or solidification reaction was detected throughout the cooling profile. The closeness in boron concentrations in ternary alloys A and C could be responsible for the similarity in their thermal properties. As presented in Fig. 2(c), the absence of any noticeable reaction during cooling in the range 800–1350 °C could be due to the absence of a melting transformation during heating cycle. The spectrum shown in Fig. 2(d) for alloy D is a close replica of spectrum obtained for sample B. As highlighted earlier, it is shown that besides Ti concentration, boron content also played a remarkable role in the thermal characteristics of these alloys. Two slight endothermic reactions were observed before the main transformation effect during heating process at 976.6 °C, 1021.6 °C, and 1113.0 °C respectively. As in alloy B, the two initial peaks correspond to the initial reaction. Conversely, during slow cooling, two successive low exothermic phase transformations are shown at 1172.6 °C and 1101.3 °C depicting the onset of solidification before the major eutectic reaction at 987.6 °C. The eutectic reaction showed that alloy D transformed into two solid phases at the same time. As shown in the thermogram, Fig. 2(e), alloy E (82Ni7B11Ti) exhibited a distinct thermal feature with no visible presence of transformation or phase change reactions during heating. The only observation is the drastic lowering of the enthalpy at the onset of second heating segment, this event could be attributed to the sudden change in the heating rate (20 K/min to 10 K/min). The same behavior was exhibited during first cooling process from 1350 °C to 800 °C, as no thermal reaction is detected. However, alloy E exhibited three successive low exothermic reactions in the second cooling segment (800–30 °C) at 476.7 °C, 579.0 °C and 685.6 °C, respectively, corresponding to low temperature recrystallization. The thermal behavior of alloy E is similar to that of alloy C, and the main feature common between them is the concentration of boron, which is nearly the same as shown in Table 1. Also, there is a similarity between the thermal reactions that occurred between alloy B and D, maybe due to the comparable amount boron in the ternary alloys which lowered the melting temperature of the alloys.

3.2. Microstructure of the alloys

The microstructure of the prepared alloys can be classified into two main groups, Ni(α) as primary phase group (alloys
A, B and C) and \( \tau \) as primary phase group (alloys D and E). Similar primary phases have been reported in related studies [1,29–31]. The thermal transformation temperatures and the possible crystallized phases formed in the alloys are presented in Table 2.

### 3.2.1. \( \text{Ni}(\alpha) \) as primary phase group
In this study, the \( \text{Ni}(\alpha) \) primary phase group are the alloys with \( \text{Ni}(\alpha) \) as their main phase, in conjunction with other eutectic structures during their solidification under cooling process. For alloy A (93Ni5SB2Ti), its solidification began with the formation of \( \text{Ni}(\alpha) \) as the primary phase at 941.4 \( ^\circ \text{C} \). The SEM micrograph of alloy A is presented in Fig. 3(a). The solidification of this alloy advanced as the temperature decreased further until the composition of the liquid reached the ternary eutectic point 1 (Fig. 1). At this point, Ni, Ni$_3$B and \( \tau \) crystallized simultaneously in agreement with the ternary reaction L → Ni + Ni$_3$B + \( \tau \). This simultaneous crystallization commenced at 881.6 \( ^\circ \text{C} \) (Fig. 2(a)). The structure of this ternary eutectic is as shown in Fig. 3(a). At a more reduced temperature, the ternary phase \( \tau \) underwent some solid-state transformation. This could be observed from the breakage of the semi-blocky structure in Fig. 3(a). It should be noted that the cooling condition applied favored controlled diffusion of all the micro-constituents in the alloy. This made the solid-state transformation to occur during slow cooling. At this point, the ternary phase \( \tau \) was likely permeated or impregnated within the atoms of nickel and titanium simultaneously. The segregation of these atoms of nickel and titanium to the boundary or coalesce gave rise to the eutectoid-like (solid-state transformation) structure as follows:

\[
\tau(\text{Ni, Ti}) \rightarrow \text{Ni}_3\text{B} + \text{Ni}(\text{Ti})
\]  

(1)

Battezzati et al. [32] and Ajao [21] reported similar observations during slow cooling Ni-hard alloy. For alloy B (85Ni12B3Ti) with a slightly higher titanium content (3 wt.%), the phases formed were similar to that of alloy A. Fig. 3(b) shows the microstructure of alloy B, while Figs. 3(d) and (e) shows the chemical compositions of \( \text{Ni}(\alpha) \) and Ni$_3$B + \( \tau \) phases in the alloys respectively. Considering the alloy behavior during heating, the presence of high content of boron lowered the transformation reaction of the alloys which started at relatively low temperatures (982.1 \( ^\circ \text{C} \) and 1026.3 \( ^\circ \text{C} \). However, the crystallization of alloy B during cooling commenced with the formation of the primary phase of \( \text{Ni}(\alpha) \) at 1167.1 \( ^\circ \text{C} \). As the temperature decreased further, the solidification of the liquid progressed until the liquid reached the ternary eutectic point 1 depicted in Fig. 1. Here, the ternary eutectic phase (Ni + Ni$_3$B + \( \tau \)) was formed at 978.0 \( ^\circ \text{C} \). Furthermore, alloy C with composition 86Ni688Ti exhibited noticeable blocky Ni (\( \alpha \)) as the primary phase. The optical image of this alloy is presented in Fig. 3(c). Ni (\( \alpha \)) phase of alloy C would have formed at a temperature within the first cooling segment, but the transformation temperature was not detected on thermogram. However, as the temperature decreased further, the solidification process advanced to the ternary point 1 as depicted in Fig. 1. Here, the ternary eutectic Ni + Ni$_3$B + \( \tau \) (Fig. 3(c)) was formed at 634.8 \( ^\circ \text{C} \). It should be noted that the absence of Ni$_3$Ti and TiB$_2$ in the microstructure of this group of alloy denoted that the solidification of this group of alloy did not get to the solidus line 2-3 (Fig. 1) [30] before the end of their solidification. The EDX results shown in Fig. 3(e) and (f) indicate the main composition of the observed phases in the alloys. Expectedly, the main element present based on the spectra peaks is nickel and average compositions of titanium. It is obvious that boron is not detected which might be due to the detection limit of the EDX equipment. Boron being a low Z element, it might not be easily detected due to the machine limitation. Other elements are detected in trace amount which are mainly due to the impurity effects.

### 3.2.2. \( \tau \) as primary phase group
In this group, the ternary phase \( \tau \) was formed as the primary phase, while other eutectic structures were also formed during the solidification of these alloys [1]. The microstructure of alloy D (80Ni13B7Ti) is presented in Fig. 4(a). As observed, alloy D has a similar behavior to that of alloy B in the heating transformation due to thermal effect of boron composition in the alloy. Sample B also exhibited early transformational peak at 976.6 \( ^\circ \text{C} \). The solidification of this alloy commenced with the crystallization of the primary ternary phase \( \tau \) at 1172.6 \( ^\circ \text{C} \). The solidification continued until the liquid reached the point 1 in Fig. 1. At this point, the ternary eutectic Ni-Ni$_3$B-\( \tau \) commenced crystallization at a temperature of 1101.3 \( ^\circ \text{C} \). With further fall in temperature during the slow cooling, the solidification of the liquid progressed until the liquid reached the solidus line 2 as depicted in Fig. 1. Then, alloy D underwent a major eutectic transformation and crystallized to form the ternary eutectic Ni-Ni$_3$Ti-\( \tau \) phase at 987.6 \( ^\circ \text{C} \). The microstructures of these phases are shown in Fig. 4(a). In the same vein, for alloy E, the primary phase formed as solidification began was the ternary phase \( \tau \). The micrograph for alloy E is shown in Fig. 4(b), while the chemical composition obtained from EDX analysis phases \( \tau \) and Ni-Ni$_3$Ti-\( \tau \) phases are shown in Figs. 4(c) and (d), respectively. From the analysis of alloy E, which is similar to alloy C in term of thermal characteristic, it is expected that its recrystallization with the
formation of the primary ternary phase \( \tau \) within the first cooling segment (800–1350 \( ^\circ \)C), but the thermal reaction was not detected on the thermogram. The \( \tau \) phase was followed by the crystallization of the ternary eutectic Ni-Ni\(_3\)B-\( \tau \) shown at 685.6 \( ^\circ \)C. These two microstructures are shown in Fig. 4(b). The apparent absence of TiB\(_2\) and Ni\(_3\)B in all the microstructural observations indicated that the phase reactions of the alloys did not get to the point 1–4 or 4–3 in Fig. 1 before the point of their final solidification. As shown in the EDX spectra, the major constituents of these phases are nickel and titanium.

4. Conclusion

In the present work, five samples of Ni-B-Ti base hard alloys with varying constituents of B and Ti contents were prepared and characterized in order to study the alloying effect of titanium on its microstructure and thermal properties. Boron was used to induce early thermal transformation reaction in the ternary alloys. The effect of high concentrations of boron in alloys was conspicuously observed during DTA heating process for samples B and D, which exhibited relatively
low temperature endothermic peaks at 982.1 °C and 976.6 °C, respectively. Titanium was added to strengthen the alloys. Two primary phases, namely Ni (ω) and τ, were detected depending on titanium concentrations via the microstructural analysis of the alloys. During slow and control cooling, major eutectic transformations were observed for Ni-B-Ti hard alloy samples with relatively higher content of boron, while eutectoid transformation of the τ phase was also reported for alloy with low Ti content (alloy A).

**Conflicts of interest**

The authors declare no conflicts of interest.

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