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Study on $TiAl_2$-based ternary (Fe or Ni) titanium aluminides

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Several ternary alloys were designed to help understand the type of substitution and the nature of transformation in $L1_2$-type ternary (Fe or Ni) titanium aluminides. X-ray powder diffraction analysis, scanning electron microscopy and microhardness measurements were used to delineate the phases present in arc-melted alloys that were annealed at 1300 K for 10 days. The results of this study show that, in $L1_2$ type ternary (Fe, Ni) titanium aluminides, Fe or Ni substitutes for Ti, and these materials are $TiAl_2$-based, contrary to previous assumptions.

1. Introduction

Ordered intermetallic compounds, especially aluminides, are currently being considered as potential materials for high-temperature applications. This is largely due to the strong bonding which leads to an invariant modulus; high activation energy for diffusion, that in turn makes diffusion-dependent mechanisms like creep and fatigue sluggish at high temperatures; and improved oxidation resistance which emanates from the large aluminium content of these materials [1]. However, intermetallic compounds have very low ductility at ambient temperatures and this still limits their extensive use as a structural material for high temperatures.

Titanium aluminides Ti_3Al, TiAl and $TiAl_3$ have the lowest density among the intermetallics currently being considered [2]. They offer considerable advantage in cases where light and strong materials are required at intermediate and high temperatures. Relative to Ti_3Al and TiAl, $TiAl_3$ has received little attention in the past. This is probably due to the limited range of solubility that renders the processing of this intermetallic compound difficult. However, $TiAl_3$ has lower density ($3.37\ g\,cm^{-3}$) and better oxidation resistance than the other two titanium aluminides [3, 4]. Like many other aluminides, $TiAl_3$ is also brittle at ambient temperatures [3].

The crystal structure of $TiAl_3$ is DO_{22}; this is an ordered, body centred tetragonal with lattice parameters of $a = 0.384$ nm and $c = 0.8596$ nm [3]. Hence the brittleness in this intermetallic compound may be attributed to this complex crystal structure which affords an insufficient number of slip systems. A possible way of overcoming this brittleness in $TiAl_3$ is to transform the DO_{22} crystal structure to the ordered face centred cubic $L1_2$ crystal structure which has a sufficient number of slip systems.

Recently, some ductility has been reported from such transformations in several ternary alloyed (Cr, Fe, Mn, . . .) '$TiAl_3$-based' intermetallics [5–13]. In all these studies it is assumed that the ternary alloying element substitutes for aluminium. However, such an assumption violates the atomic radius ratio criterion [14], which was developed by Van Vucht and Buschow for rare-earth trialuminides [15, 16]. According to this criterion, in an AB_3-type rare-earth trialuminide, the structure becomes more hexagonal as the atomic radius ratio r_A/r_B increases. If we assume the same criterion to be also true for transition metal trialuminides, then the addition for Cr, Fe, Mn, . . . to $TiAl_3$, which have smaller radii than aluminium, we should obtain non-cubic structures instead of an ordered, cubic $L1_2$ crystal structure as reported in the literature [17–20, 9–13].

This apparent conflict can be resolved if we assume that the ternary alloying element, Cr, Fe, Mn etc., in $TiAl_3$ substitutes for titanium instead of aluminium. If this is the case, then the analysis of compositions of $L1_2$ type and $TiAl_3$-based titanium aluminides lead us to another important question about the nature of these materials [14]. In other words, are these $L1_2$ type titanium aluminides $TiAl_3$-based as commonly accepted in the literature so far, or are they $TiAl_2$-based intermetallics? Hence the main objective of this study was to understand the above two premises in Fe or Ni ternary alloyed $L1_2$-type titanium aluminides.

2. Experimental procedure

Six alloy buttons (100 g) of the compositions $Ti_{34-x}Fe_xAl_{66}$ and $Ti_{34-x}Ni_xAl_{66}$ ($x = 1, 4, 8$ at %) were prepared by arc melting of high-purity metals in an argon atmosphere on a water-cooled copper hearth. In order to achieve homogeneity, the alloys were melted several times. Since very little weight loss was reported ($< 0.02\%$) after melting, the compositions were assumed to be as given above.

The alloys (~ 30 g) were annealed 10 days at 1300 K in a vacuum of 1×10^{-5} torr and then furnace cooled. Each sample was pulverized to < 325 mesh, wrapped in high purity Ti foils, and annealed at 973 K

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for 4 h in a vacuum of 1×10^{-5} torr. The X-ray powder diffraction (XRD) patterns were obtained with a computer controlled Philips diffractometer using Cu K_α radiation. All patterns were obtained at a speed of 1° $\min^{-1}$ with a step scan size of 0.05°.

Metallographic examination of the samples were made by optical metallography and scanning electron microscopy (SEM). Microhardness measurements were obtained at 1 kg load with a dwell time of 15 s.

3. Experimental results and discussion

A summary of the phases observed by XRD analysis and microhardness of alloys annealed at 1300 K for 10 days is given in Table I. The alloys with 1 at % Fe and Ni is primarily single phase $TiAl_2$. As the amount of the ternary alloying element Fe or Ni is increased to 4 at %, a two phase microstructure composed of $TiAl_2$ and $L1_2$ is observed (Fig. 1). X-ray powder diffraction data for these two alloys is given in Table 2 and Table 3. Further increase of the ternary alloying element Fe or Ni lead to primarily one phase microstructure of $L1_2$ [22].

As given in Table I, the microhardness of alloys decrease from 390 to 260 with increasing ternary alloying element Fe or Ni. The microhardness values of the primarily single-phase $TiAl_2$ alloys is found to be lower than that of $TiAl_3$, which has been reported

TABLE I Summary of the phases observed and microhardness values (Vickers hardness number) of the ternary Al–Ti–Fe and Al–Ti–Ni alloys annealed at 1300 K for 10 days

Alloy	Phases	VHN (1 kg, 15 s)
$Ti_{33}Fe_1Al_{66}$	$TiAl_2$	393
$Ti_{33}Ni_1Al_{66}$	$TiAl_2$	390
$Ti_{30}Fe_4Al_{66}$	$TiAl_2$, $L1_2$	343
$Ti_{30}Ni_4Al_{66}$	$TiAl_2$, $L1_2$	368
$Ti_{26}Fe_8Al_{66}$	$L1_2$	257
$Ti_{26}Ni_8Al_{66}$	$L1_2$	287

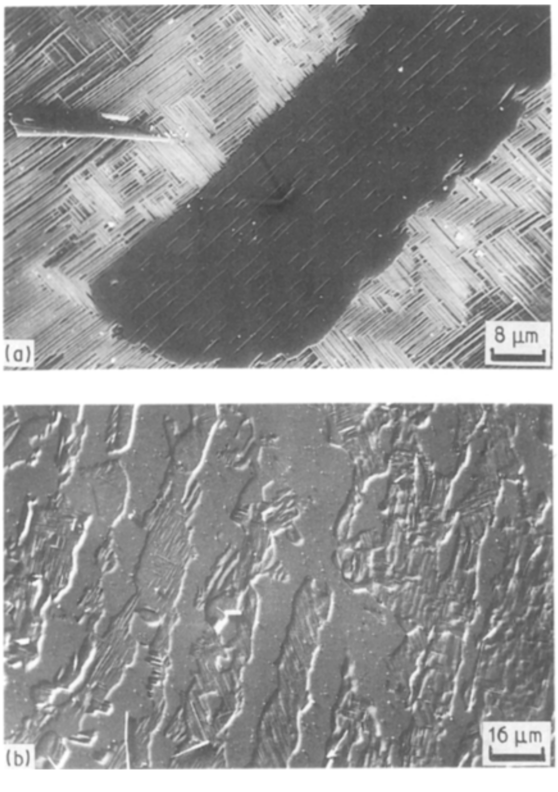

Figure 1 Two-phase microstructure of the samples annealed at 1300 K for 10 days. (a) $Ti_{30}Fe_4Al_{66}$; (b) $Ti_{30}Ni_4Al_{66}$.

TABLE II XRD data for $Ti_{30}Fe_4Al_{66}$, annealed at 1300 K for 10 days

$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$[a]	Reflection	I/I_o(%)	Phase
0.0383	0.0381	0 0 1	4	$L1_2$
0.0387	0.0387	0 1 1	4	$TiAl_2$
0.0763	0.0761	0 1 1	2	$L1_2$
0.0870	0.0869	0 1 7	3	$TiAl_2$
0.1116	0.1116	1 1 6	100	$TiAl_2$
0.1144	0.1142	1 1 1	58	$L1_2$
0.1174	–	–	3	[d]
0.1190	0.1191	0 1 9	2	$TiAl_2$
0.1447	0.1447	0 0 12	20	$TiAl_2$
0.1509	0.1508	0 2 0	33	$TiAl_2$
0.1524	0.1523	0 0 2	31	$L1_2$
0.1907	0.1904	0 1 2	2	$L1_2$
0.2075	0.2075	0 1 13	2	$TiAl_2$
0.2884	0.2890[b]		2	$TiAl_3$
0.2955	0.2955	0 2 12	19	$TiAl_2$
0.3019	0.3015	2 2 0	11	$TiAl_2$
0.3051	0.3046	0 2 2	14	$L1_2$
0.3976	0.3979[c]	1 1 3	3	Al
0.4012	0.4010	1 1 18	9	$TiAl_2$
0.4134	0.4131	1 3 6	18	$TiAl_2$
0.4196	0.4188	1 1 3	14	$L1_2$
0.4467	0.4463	2 2 12	8	$TiAl_2$
0.4576	0.4569	2 2 2	5	$L1_2$

[a] For $TiAl_2$, $\sin^2\theta_{calc}$ is taken from [21] where $a = 0.3971$ nm and $c = 2.432$ nm, for $L1_2$ it is calculated from experimentally determined lattice constant $a = 3.951 + 0.002$ nm.

[b] From JCPDS No. 37 1449.

[c] From JCPDS No. 40 787.

[d] Unidentified.

TABLE III XRD data of $Ti_{30}Ni_4Al_{66}$, annealed at 1300 K for 10 days

$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$[a]	Reflection	I/I_o(%)	Phase
0.0386	0.0384	0 0 1	4	$L1_2$
0.0868	0.0869	0 1 7	2	$TiAl_2$
0.1115	0.1115	1 1 6	100	$TiAl_2$
0.1149	0.1151	1 1 1	36	$L1_2$
0.3660	—	—	3	[c]
0.1444	0.1447	0 0 12	18	$TiAl_2$
0.1510	0.1508	0 0 2	26	$TiAl_2$
0.1532	0.1537	0 0 2	17	$L1_2$
0.1599	0.1600[b]		3	$TiAl_3$
0.1921	0.1919	0 1 2	3	$L1_2$
0.2955	0.2955	0 2 12	16	$TiAl_2$
0.3020	0.3015	2 2 0	9	$TiAl_2$
0.3072	0.3070	0 2 2	8	$L1_2$
0.4009	0.4010	1 1 18	9	$TiAl_2$
0.4138	0.4131	1 3 6	14	$TiAl_2$
0.4224	0.4222	1 1 3	7	$L1_2$
0.4468	0.4463	2 2 12	7	$TiAl_2$
0.4610	0.4605	2 2 2	2	$L1_2$

[a] For $TiAl_2$, $\sin^2\theta_{calc}$ is taken from [21] where $a = 0.3971$ nm, $c = 2.432$ nm, for $L1_2$ it is calculated from experimentally determined lattice constant $a = 0.3935 \pm 0.004$ nm.

[b] From JCPDS No. 371 449.

[c] Unidentified.

to be around 500 at 25 g load [23]. The microhardness of the single phase $L1_2$ alloys is found to be higher than the values (around 200) reported in the literature [13]. This difference may be attributed to the solid-solution hardening effect due to the slightly higher amount of Ti in the alloys used in this study.

Within the context of alloying variables and the current work on $L1_2$-type ternary titanium aluminides, these experimental results can be evaluated in the following way. In AB_3-type ordered intermetallics, alloying variables such as electron concentration (e/a) and atomic radius ratio (r_A/r_B) have been shown to change the crystal structure. According to Sinha [24, 25], a transition from the ordered cubic structure to ordered hexagonal structure occurs as the e/a is increased. A similar transition has been observed by Van Vucht and Buschow in rare earth trialuminides with an increase in r_A/r_B [15, 16]. Now let us examine these two alloy variables for $L1_2$ type and $TiAl_3$-based ternary titanium aluminides.

If we define the electron concentration as 'the average per atom of the number of electrons outside inert gas shells' [24], then an increase in e/a is expected on addition of ternary alloying elements Cr, Mn, Fe, Co, Ni, Cu, or Zn into $TiAl_3$, since all these elements have a higher number of electrons than Ti and Al at their outer inert shells. Hence, assuming the e/a criterion to be also valid for ternary $L1_2$-type titanium aluminides, then we should expect the formation of ordered hexagonal structures rather than of the ordered cubic structures that are reported in the literature. This apparent conflict can be resolved in two ways. The first is based on redefining electron concentration as 'the number of electrons in excess of the last complete shell' [26]. In this case, since the e/a of these elements corresponds to zero for Fe, Co, and Ni, one for Cu, and two for Zn, addition of these elements to $TiAl_3$ will reduce the electron concentration with the consequence of attaining more cubic structures. Hence, within this terminology, the $L1_2$-type structures observed in TiM_xAl_{3-x}, where M is Fe, Co, Ni, Cu, or Zn and x varies from 8 to 12.5 at %, can be explained by the reduction in electron concentration. However, even such a redefinition of e/a cannot explain the recently observed $L1_2$ phases in Al–Ti–Cr and Al–Ti–Mn systems because of the high e/a for Cr and Mn that should lead to ordered hexagonal structures. The second means of resolving the problem is to use the atomic radius criterion as the effective alloy variable in $L1_2$-type ternary titanium aluminides. In this case, if we assume that the ternary alloying element (Cr, Mn, Fe, Co, Ni, Cu, or Zn) substitutes for Ti rather than Al, the latter being assumed in the literature so far, then a decrease in atomic radius will occur due to smaller Goldschmidt atomic radius of the above ternary transition metals than Ti. Such a decrease in atomic radius ratio leads to more cubic structures and explains the presence of the ordered cubic structures in these ternary titanium aluminides.

The above discussion on the validity of the atomic radius ratio criterion also leads us to another point about the nature of these ternary $L1_2$-type titanium aluminides. The stoichiometry of these alloys shows that, if the ternary alloying element substitutes for Ti, then these alloys are $TiAl_2$-based rather than $TiAl_3$-based. Our research was based on these two premises: firstly the validity of the atomic radius ratio criterion, where ternary alloying element is thought to substitute for Ti; and secondly the notion that these $L1_2$-type ternary titanium aluminides are $TiAl_2$-based rather than $TiAl_3$-based. The alloys designed for testing these two premises showed that addition of Fe or Ni to $TiAl_2$, where ternary alloying element substitutes for Ti, first led to a two-phase mixture of $TiAl_2 + L1_2$ and then to single phase $L1_2$ at higher amounts of Fe or Ni. These results emphasize the importance of geometrical considerations in determining the phase stability of $L1_2$-type ternary titanium aluminides.

4. Conclusions

1. The transition elements Fe or Ni substitute for Ti in $L1_2$-type ternary titanium aluminides.
2. The $L1_2$-type ternary aluminides of Fe and Ni are $TiAl_2$-based.

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