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Mechanical properties of Cr, Mn, Fe, Co, and Ni modified titanium trialuminides

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To increase gas turbine efficiency, new high-temperature-resistant and lightweight materials are needed. Titanium trialuminides are an interesting option, but they are currently too brittle at room temperature to be used as turbine blades. Brittleness of $TiAl_3$ can be reduced by alloying with several transition metal elements. The effect of ternary additions of Cr, Mn, Fe, Co, or Ni at various stoichiometries (3 to 9 at.%) to the intermetallic $TiAl_3$ is studied by metallography, X-ray diffraction and three-point-bend testing. These methods indicate that the 6 at.% Cr or Co additions give the highest flexural strength with only a small trade-off in failure strain when compared to the 9 at.% additions of chromium and manganese.

1. Introduction

The efficiency of gas turbine engines would be improved by the integration of lightweight and high-temperature-resistant materials in the design of turbine blades and turbine guide vanes. The currently used superalloys have a high density, and therefore, new materials are being sought that combine low mass and good mechanical properties. To improve on parts used for high-temperature components, the new materials must exhibit improved resistance to heat, creep, and oxidation, coupled with good strength and lower mass [1]. Titanium trialuminide ($TiAl_3$) is attractive as such a material, but its tetragonal unit cell makes it very brittle at room temperature [2]. Under compression $TiAl_3$ exhibits some degree of deformation, while under tension brittle failure occurs rapidly [3].

If the tetragonal crystal structure of binary $TiAl_3$ is transformed into one with higher symmetry, it may be possible to reduce this inherent brittleness. For $TiAl_3$, alloying can change the crystal structure [4] from $D0_{22}$ to $L1_2$, which exhibits a crystal structure of higher symmetry and has 5 slip systems (the minimum needed for a ductile material as stated in the von Mises criterion) [5]. Elements that make this transformation possible are chromium, manganese, iron, cobalt, nickel, copper, zinc, rhodium, palladium, silver, gold, and platinum [6]. The alloying elements for this study were chosen with a view of obtaining the lowest possible weights for the final intermetallic, and consist of the five 3d period elements: Chromium, manganese, iron, cobalt, or nickel.

Melting elementary constituents at the correct concentrations to form the $L1_2$ does not result in a homogeneous compound due to incongruent melting of the $L1_2$ phase [6]. In the chromium-modified intermetallic, the casting process results in secondary phases distributed in an $L1_2$ matrix. One of these secondary phases is $Al_{17}Cr_9$, which leads to porosity during subsequent homogenization treatments [7]. This is also observed in the processing of the other ternary additions (e.g., Al_8Mn_5 in the Al-Ti-Mn system) [6].

At this point it should be mentioned that superalloys have been developed over the last 80 years [8] and are at peak performance, whereas intermetallics have been studied in depth for only about 15–20 years. Gamma titanium aluminides have already been implemented in the jet turbine engines of the F-22 jet fighter, and jet engine compressor disks have been made of Ni_3Al [9].

2. Experimental procedure

Thirteen 250 g alloy buttons were cast in a nonconsumable arc furnace, re-melted twice and then homogenized by heat treatment at 1200°C for 7 days. The elementary metals consisted of pellets or chips of at least 99.9% purity, and were weighed to 0.1 g accuracy for each metal.

The compositions produced correspond to: $Ti_{31}X_3Al_{66}$, $Ti_{28}X_6Al_{66}$, $Ti_{25}X_9Al_{66}$, $Ti_{30}Y_4Al_{66}$, and $Ti_{26}Y_8Al_{66}$ with X = Cr, Mn or Co, and Y = Fe or Ni. The different amounts for iron and nickel were chosen for ease of comparison with our previous study [5].

In addition, sections of all homogenized specimens (with the exception of those with the three percent ternary additions) underwent a long-term heat treatment at 500°C for four weeks, to determine if the $L1_2$ phase is stable.

The grain structure was observed after etching with a solution consisting of 10 ml HF, 15 ml HNO_3, and 50 ml glycerin [5]. Vickers hardness was found with a Leco M-400 hardness tester (1 Kg, 20 s).

Three-point-bend testing was adapted from the ASTM standard C1161-94, in that the bend bars were scaled down to half size due to the condition of the intermetallic buttons that made larger bars impossible. The bend bars were electro-discharge machined, followed by grinding and polishing, with a final finish of 0.3 microns. The edges were slightly beveled with 600 grit sandpaper. Displacement of the cross-head was at 1 μm/s and data were sampled at 100 points/s. Due to the small displacements, a lot of noise is present in the data log. From this data stress and strain at failure was calculated for the tensile side.

3. Results and discussion

In order to design turbine blades that improve upon existing superalloys, intermetallics are needed that combine several properties. The most important combination of properties is that of low weight with high-temperature-resistance. In this study, the properties of strain to failure, flexural strength and hardness were evaluated for ternary additions of Cr, Mn, Fe, Co, or Ni at room temperature. The important criterion of low density was calculated from the lattice parameters obtained from XRD [10].

Four of the materials prepared in this study were selected for discussion (the selection was based on the best combination of strength and strain to failure). Table I summarizes the results for the three-point-bend testing.

Table II compares the best compositions to representative superalloys. The selected intermetallics have a density of only 40–45% of that of the superalloys. Considerable porosity is observed in the high chromium- or manganese-containing compounds ($Ti_{25}Cr_9Al_{66}$ and $Ti_{25}Mn_9Al_{66}$), which possibly has a deleterious effect on the bend-testing results. Microcracks may also contribute to the fracture behavior. The medium chromium or cobalt stoichiometries ($Ti_{28}Cr_6Al_{66}$ and $Ti_{28}Co_6Al_{66}$) show an almost twofold increase in strength, compared to the high chromium and manganese ternary addition intermetallics, with approximately 25% less strain to failure and much less porosity. The failure strength of the medium chromium- and cobalt-containing intermetallics is similar to the yield strength of Stellite and Hastelloy, but strain to failure is considerably less.

In terms of fracture behavior, the flexural-strength specimens show a rough, torn surface for the high manganese-containing material (Fig. 1), which exhibited some yielding before failure, and a much smoother fracture surface for the high chromium-containing intermetallic (Fig. 2), which exhibited no yielding. The

TABLE I Summary of collected data of studied intermetallics

Composition	Failure σ (MPa)	Failure ε (mm/mm)	Displacement (mm)	Yield σ (MPa)	Yield ε (%)
$Ti_{31}Cr_3Al_{66}$	111.5	0.0011	0.016	–	–
$Ti_{28}Cr_6Al_{66}$	502.5	0.003	0.053	–	–
$Ti_{25}Cr_9Al_{66}$	265	0.0037	0.049	–	–
$Ti_{28}Mn_6Al_{66}$	337.5	0.003	0.043	–	–
$Ti_{25}Mn_9Al_{66}$	290	0.004	0.066	165	0.14
$Ti_{30}Fe_4Al_{66}$	130	0.0015	0.021	–	–
$Ti_{26}Fe_8Al_{66}$	87.5	0.0008	0.013	–	–
$Ti_{28}Co_6Al_{66}$	460	0.0028	0.038	–	–
$Ti_{25}Co_9Al_{66}$	225	0.0019	0.027	–	–
$Ti_{30}Ni_4Al_{66}$	125	0.0013	0.018	–	–
$Ti_{26}Ni_8Al_{66}$	195	0.0019	0.025	–	–

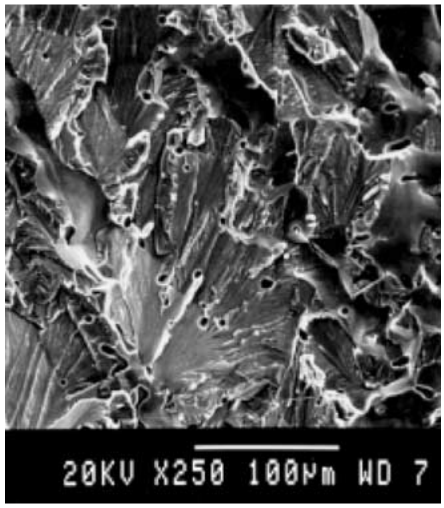

Figure 1 Fracture surface of $Ti_{25}Mn_9Al_{66}$. This is the only composition that showed yielding during flexural strength testing. Note the high amount of porosity.

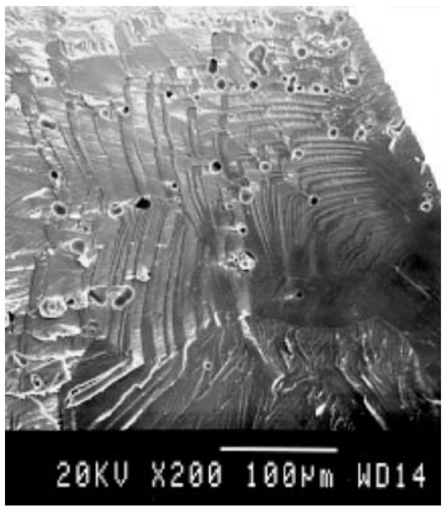

Figure 2 Fracture surface of $Ti_{25}Cr_9Al_{66}$. This composition exhibited no yielding. Note the high amount of porosity.

TABLE II Comparison of the best performing intermetallics and representative superalloys (superalloy data from reference 11)

Composition	Density (g/ccm)	Porosity Volume %	Hardness VHN	Yield σ (MPa)	Failure σ (MPa)	Failure ε (%)
$Ti_{25}Cr_9Al_{66}$	3.69	2.3	165	–	265	0.37
$Ti_{25}Mn_9Al_{66}$	3.72	2	147	165	290	0.4
$Ti_{28}Co_6Al_{66}$	3.66	0.11	470	–	460	0.3
$Ti_{28}Cr_6Al_{66}$	3.64	0.23	373	–	503	0.3
Inconel	8.22	–		875	1275	25
Stellite 21	8.31	–	244	517	724	9
Hastelloy B2	9.22	–	220	412	894	61

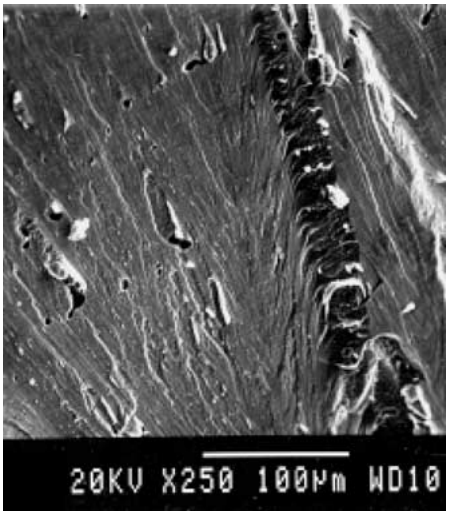

Figure 3 Fracture surface of $Ti_{28}Co_6Al_{66}$. This composition shattered into many fragments upon failure.

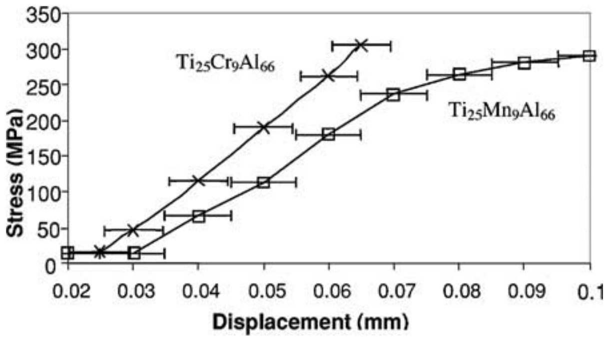

Figure 4 Stress vs. displacement plot of $Ti_{25}Cr_9Al_{66}$ and $Ti_{25}Mn_9Al_{66}$.

medium cobalt-alloyed material failed by shattering into many small fragments, and its fracture surface displays even smoother features (Fig. 3), demonstrating this composition's very high brittleness. All other specimens failed in a similar manner to that of the high chromium-containing intermetallic.

The high chromium and manganese stoichiometries show a much lower strength than the superalloys, but are still attractive because of the appreciably high strain to failure of the tested intermetallics.

The high manganese-containing material is the only one in this study that exhibited yielding (Fig. 4) at room temperature. The high chromium-containing intermetallic does not exhibit any yielding (Fig. 4). Kumar and Brown [12] report that $Ti_{25}Mn_9Al_{66}$ exhibits higher tensile elongation (i.e., strain) than $Ti_{25}Cr_9Al_{66}$ between 600 K and 900 K. No data has been reported for lower temperatures, but the reported data back up the observation in this work of higher strain to failure for the high manganese-containing material compared to the high chromium-containing intermetallic. Another factor causing lower strain to failure in the high chromium-containing materials could be the small amount of $TiAl_2$ phase that is detected by XRD, whereas no $TiAl_2$ was found in $Ti_{25}Mn_9Al_{66}$.

The high chromium and manganese ternary addition compounds show low failure strength relative to the yield strength of superalloys. Superalloy strength decreases with increasing temperature (Fig. 5), whereas

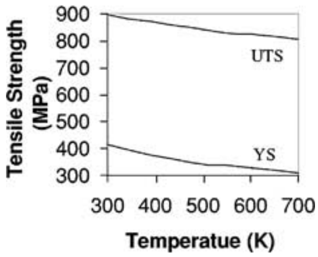

Figure 5 Tensile strength vs. temperature for Hastelloy [11].

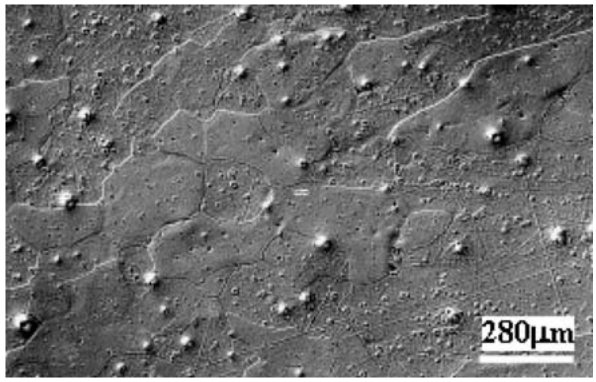

Figure 6 Microstructure of $Ti_{25}Cr_9Al_{66}$.

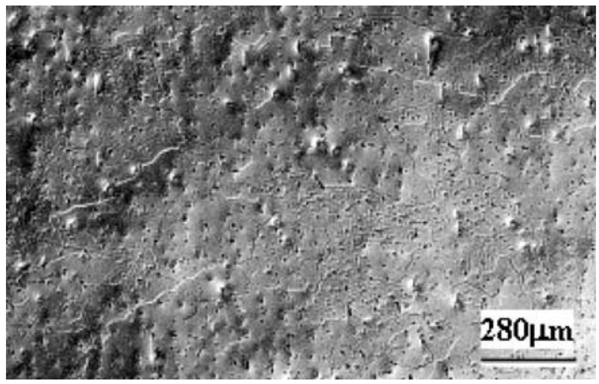

Figure 7 Microstructure of $Ti_{25}Mn_9Al_{66}$.

the strength of these intermetallics remains stable or even increases at elevated temperatures [13] and fracture toughness increases as well [14]. Kumar *et al.* [13] and Mabuchi *et al.* [7] report similar stress and strain data for $Ti_{25}Mn_9Al_{66}$. Kumar *et al.* [13] also report no yielding in bend-testing of forged $Ti_{25}Cr_8Al_{67}$ at room temperature, but find in a more recent study [15] that a heat treatment after forging can lead to a plastic strain to about 0.6% at slightly elevated temperatures (473 K).

The medium ternary additions of chromium and cobalt produced compounds with higher strength and hardness, but slightly less strain to failure than the high chromium and manganese ternary addition compounds. The hardness of the compounds with a medium ternary addition of chromium and cobalt is also superior to the superalloys. The higher strength can be explained by the presence of about 33% $TiAl_2$ (from stoichiometry) and a different microstructure as compared to the compositions exhibiting only the $L1_2$ crystal structure. The materials with a high ternary addition of chromium or manganese ($Ti_{25}Cr_9Al_{66}$ and $Ti_{25}Mn_9Al_{66}$) exhibit a similar microstructure of roughly equiaxed grains (Figs 6 and 7), whereas $Ti_{28}Cr_6Al_{66}$ shows small grains

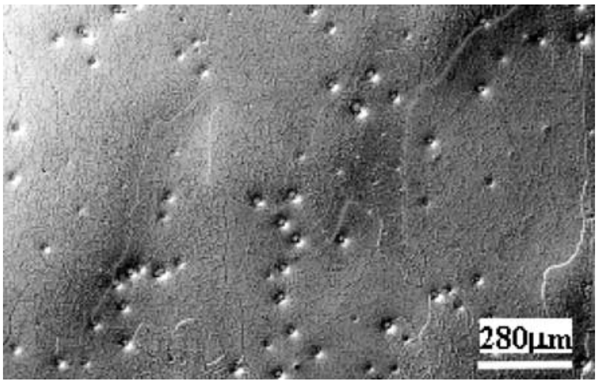

Figure 8 Microstructure of $Ti_{28}Cr_6Al_{66}$.

Figure 9 Microstructure of $Ti_{28}Co_6Al_{66}$.

arranged within larger grain-arrays (Fig. 8), but this compound does not exhibit a two-phase structure. The medium cobalt-containing intermetallic displays a multiphase structure with a variety of grain size and dimensions (Fig. 9), which is probably due to the presence of Ti_9Al_{13} and an unidentified phase aside from the expected $L1_2$ and $TiAl_2$ compounds [16].

All specimens show a change in grain morphology upon heat treatment. Often a highly cored and dendritic structure exists in the as-cast specimens, which disappears during the homogenization treatment.

Although only the high manganese-containing material exhibits yielding upon flexural-strength-testing, all intermetallics exhibit some inherent ductility (in the as-cast and homogenized condition). This ductility can be inferred from slip traces that are visible around Vickers indentation sites (Fig. 10). The intermetallics with high ternary additions of chromium, manganese, iron or nickel, as well as the medium ternary additions of chromium or manganese, exhibit no cracks at the Vickers indentations, unlike the other compositions. The area covered by slip traces tends to increase with increasing concentration of the ternary element, with iron and cobalt as notable exceptions. These slip traces are also correlated with decreasing hardness, except in the case of iron. The relationship of hardness and ternary element addition is summarized in Fig. 11. The hardness of the high ternary addition compounds compares very well with published values [5, 17], only the iron and cobalt modified intermetallics exhibit a higher hardness.

With increasing concentration of ternary element, the crystal structure changes from $HfGa_2$ ($TiAl_2$) to $L1_2$.

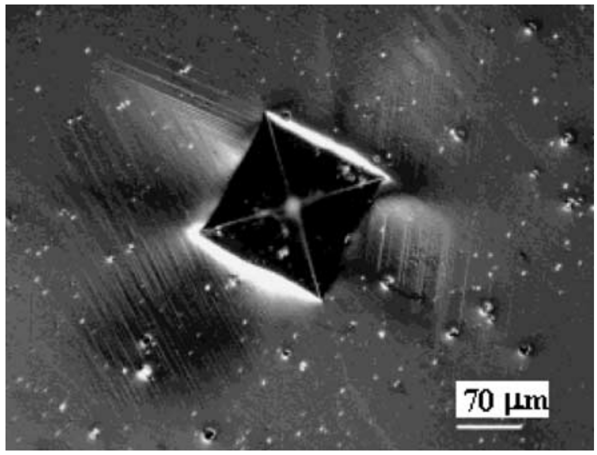

Figure 10 Slip traces around a Vickers indentation in $Ti_{25}Cr_9Al_{66}$.

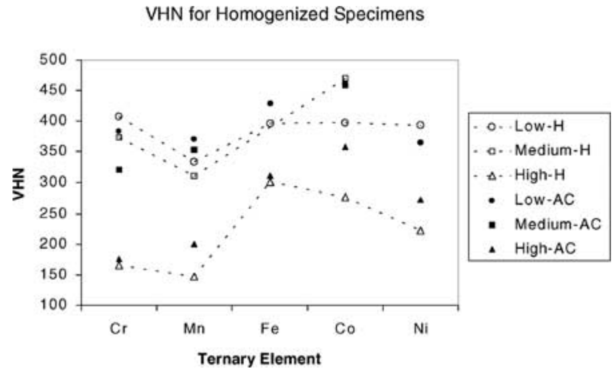

Figure 11 Vickers hardness for all specimens (H = homogenized at 1200°C, 1 week; AC = as-cast).

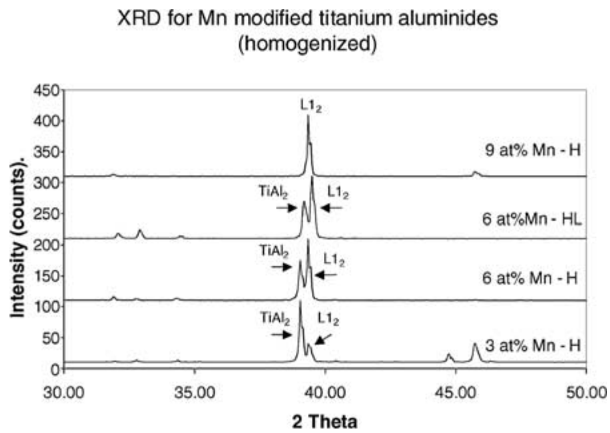

Figure 12 Section of XRD pattern for the homogenized manganese-containing specimens showing $TiAl_2$ to $L1_2$ transformation with increasing concentration of ternary addition (H = homogenized, HL = homogenized plus long-term treatment, full peak identification can be found in reference 16).

This can be clearly seen in the XRD profiles for all ternary elements tested except for iron. The spectrograph for the ternary additions of manganese can be seen in Fig. 12 (only the $L1_2$ and $HfGa_2$ strongest intensity peaks are labeled, for a full listing of all peaks see [16]). The high iron-containing intermetallic ($Ti_{26}Fe_8Al_{66}$) shows an anomalous spectrum, the ratio of $TiAl_2$ to $L1_2$ is opposite to what is expected.

The long-term heat treatment shows no change in the $L1_2$ phase, as can be seen in the XRD spectrographs for all specimens (the three percent ternary additions were not tested). The grain size increased twofold for most compositions with the exception of the cobalt 6 at.% addition specimen. The low amount of grain growth in this composition may be relevant for high-temperature applications. This characteristic, combined with the remarkably high strength (only $Ti_{28}Cr_6Al_{66}$ has a slightly higher strength) observed in this compound, makes it particularly interesting.

4. Conclusion

Present-day requirements for high fuel-efficiency engines drive the design and development of superalloys and intermetallics. The intermetallics are a relatively recent addition to the family of advanced materials that may fulfill the requirements for high-temperature-resistance combined with low specific gravity. This study investigated the ternary additions of five transition metal elements (Cr, Mn, Fe, Co, or Ni) to $TiAl_2$ alloys with the objective of obtaining a high proportion of the more ductile $L1_2$ crystal structure with $TiAl_2$ distributed for strengthening effect. Four of the compounds tested were found to show a good combination of desirable properties, especially with respect to strength and light weight. These are the medium ternary additions of chromium and cobalt, and the high ternary additions of chromium and manganese, which all show good estimated strain values and good strength. The six percent ternary addition compositions exhibit a higher strength than the nine percent ternary addition materials, with only a slightly smaller strain to failure. The six percent cobalt-containing intermetallic fails catastrophically, as do the medium and high chromium-containing specimens, but the cobalt-containing material is the most brittle. All specimens prepared (as-cast and homogenized) showed some degree of ductility as evidenced by slip traces. It must be noted that all specimens also showed many casting defects, as well as severe cracking and their strain to failure is lower than that of the superalloys. The mechanical properties of these four specimens may be greatly improved if the grain size can be refined (especially for the ones showing non-equiaxed grains), and if the porosity is reduced. Nevertheless, several of the studied ternary titanium trialuminides look promising as future turbine blade or guide vane materials.

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