

## Review

# Strategies for improving ductility of ordered intermetallics

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## Abstract

Ordered intermetallics possess attractive high-temperature properties; however, low ductility and brittle fracture limit their use as engineering materials in many cases. This paper provides a comprehensive review on the recent progress in the development of ductile ordered intermetallics and summarizes the strategies used to improve the tensile ductility of ordered intermetallics, including control of ordered crystal structures, engineering grain-boundary structure and chemistry, eliminating environmental embrittlement, microstructure optimization, control of phase stability, and promoting transformation-/twining-induced plasticity. The basic ideas and related mechanisms underlying these ductilizing strategies are discussed. In addition, a brief mention of the current use of intermetallic alloys for structural and corrosion applications is made. © 2016 The Authors. Production and hosting by Elsevier B.V. on behalf of Chinese Materials Research Society. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

**Keywords:** Ordered intermetallics; Ductility; Ductilizing strategy; Microstructure; Alloy design

## 1. Introduction

Ordered intermetallics constitute a unique class of metallic materials that form long-range-ordered crystal structures below a critical ordering temperature. This class of materials are now being widely investigated as potential high-temperature structural materials due mainly to their attractive properties, including good high-temperature strength, resistance to oxidation and corrosion, relatively low material density and high melting point [1–9]. Unlike conventional or disordered alloys whose yield strengths decrease with increasing test temperature, many ordered intermetallics exhibit an increase, rather than a decrease, in yield strength with increasing test temperature. In addition, their long-range order produces stronger bonding and closer packing between atoms, which restricts the atom mobility and generally leads to slower diffusion processes and better creep resistance in ordered lattices [10]. These unique properties of ordered intermetallics making them

very attractive for high-temperature structural and corrosion applications [11–13].

Most intermetallic alloys, however, exhibit brittle fracture and low tensile ductility at ambient temperatures, which severely restricts their practical applications as structural materials [14]. In addition, many intermetallics based on aluminides are sensitive to moisture in the environment at lower temperatures [15,16]. For the past several decades, a great deal of effort has been devoted to understanding the brittle fracture and embrittlement mechanism of the intermetallic alloys. As a result, both intrinsic and extrinsic factors that embrittle the intermetallic alloys have been identified. In parallel, a substantial body of work has attempted to improve the ductility of ordered intermetallics through application of physical metallurgical principles, which leads to the development of a variety of advanced ordered intermetallics with a good combination of high strength and high ductility for many industrial applications.

The purpose of this paper is to review the recent progress in the development of ductile ordered intermetallics and summarizes the scientific strategies used to improve the tensile ductility of ordered intermetallics, including control

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of ordered crystal structures, engineering grain-boundary structure and chemistry, eliminating environmental embrittlement, microstructure optimization, control of phase stability, and promoting transformation-/twinning-induced plasticity. These strategies can serve as useful guidelines for the alloy design of new high-strength and high-ductility intermetallic alloys in the future. Finally, a brief mention of the current use of intermetallic alloys for structural and corrosion applications in industries is given at the end of this review paper.

## 2. Control of ordered crystal structures

One of the principal obstacles to the room-temperature tensile ductility of many ordered intermetallics is the low-symmetry crystal structures that have an insufficient number of independent slip systems. It has been found that the ductility of these intermetallics can be substantially improved by control of the ordered crystal structures, that is, changing the crystal structure from low symmetry (such as ordered hexagonal structure) to high symmetry (such as ordered cubic structures) through composition modifications.

One classic example is control of the ordered crystal structures of the quasiternary system of  $\text{Ni}_3\text{V}$ – $\text{Co}_3\text{V}$ – $\text{Fe}_3\text{V}$  through adjusting the electron concentrations. It is known that the ordered structures of  $\text{A}_3\text{B}$  intermetallics are built from the regular stacking of the close packed ordered layers, either being of triangular (T) type or rectangular (R) type. Stacking of the T layers gives ordered structures with a cubic or hexagonal symmetry depending on the stacking sequence, while stacking of R layers generally form ordered structures with a tetragonal symmetry. Beck and Dwight [17,18] noted a general correlation between the stacking character of the T layers with the electron concentration ratio ( $e/a$ , the number of valence electrons per atom) in the  $\text{A}_3\text{B}$  intermetallic alloys. With an increase in  $e/a$ , the ordered structure changes from predominantly cubic to predominantly hexagonal stacking. Further increase in  $e/a$  leads to a change in the basic layer structure from T to R type [17–19]. Liu and Inouye [20,21] found that the ordered crystal structure of the  $\text{Ni}_3\text{V}$ – $\text{Co}_3\text{V}$ – $\text{Fe}_3\text{V}$  alloys can be altered systematically by controlling the electron concentration ratio, where the  $e/a$  is taken as 9, 8, 7, and 5 for Fe, Co, Ni, and V, respectively. As shown in Fig. 1, the binary  $\text{Co}_3\text{V}$  alloy forms a six-layered hexagonal ordered structure with a hexagonality of 33.3% [21]. The electron concentration ratio in  $\text{Co}_3\text{V}$  ( $e/a=8$ ) can be increased by partial replacement of Co ( $e/a=9$ ) with Ni ( $e/a=10$ ), forming ternary  $(\text{Co},\text{Ni})_3\text{V}$  alloys. With increase of  $e/a$  from 8 to 8.54, the hexagonality of the ordered structure increases step by step from 33.3% to 66.7% and finally to 100%. Further increase in  $e/a$  above 8.54 produces a change in the basic layer structure from T to R type, which gives rise to a tetragonal ordered structure similar to  $\text{Ni}_3\text{V}$  ( $\text{DO}_{22}$ ) [20,21]. On the other hand, the  $e/a$  in  $\text{Co}_3\text{V}$  can be reduced by partial substitution of Fe ( $e/a=8$ ) for Co ( $e/a=8$ ), forming ternary  $(\text{Co},\text{Fe})_3\text{V}$  alloys. When the  $e/a$  is below 7.89, the  $\text{L}_{12}$  ordered cubic structure having the stacking sequence ABC is stabilized in the  $(\text{Co},\text{Fe})_3\text{V}$  alloys. Thus, control of the electron concentration ratio provides an elegant way for alloy design. As Co is an expensive elements, the cost of the  $(\text{Co},\text{Fe})_3\text{V}$  alloys can be significantly reduced by replacing Co with less expensive elements (e.g., Fe and Ni). Considering that the  $e/a$  of Fe, Co, and Ni are 7, 8, and 9, respectively, Co in the  $(\text{Co},\text{Fe})_3\text{V}$  alloy can be replaced by an equal amount of an equiatomic mixture of Ni and Fe, which alters the alloy composition but not  $e/a$ . As long as the electron concentration falls roughly in the same range as  $(\text{Co},\text{Fe})_3\text{V}$ , the ordered cubic structure remains stable in the  $(\text{Ni},\text{Co},\text{Fe})_3\text{V}$  alloys. Eventually, all Co atoms can be replaced by Ni and Fe atoms, leading to the formation of  $\text{L}_{12}$  ordered cubic alloys of the composition  $(\text{Ni},\text{Fe})_3\text{V}$  without any Co elements [20,21].

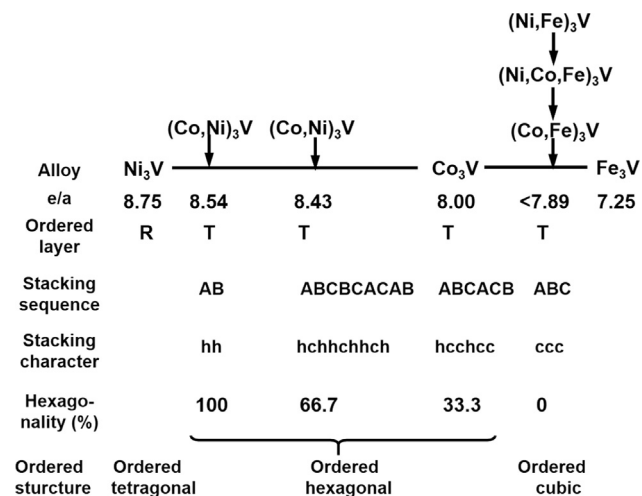


Fig. 1. Effect of electron concentration ( $e/a$ ) on the stability of ordered crystal structures in the  $\text{Ni}_3\text{V}$ – $\text{Co}_3\text{V}$ – $\text{Fe}_3\text{V}$  alloys [21].

Thus, control of the electron concentration ratio provides an elegant way for alloy design. As Co is an expensive elements, the cost of the  $(\text{Co},\text{Fe})_3\text{V}$  alloys can be significantly reduced by replacing Co with less expensive elements (e.g., Fe and Ni). Considering that the  $e/a$  of Fe, Co, and Ni are 7, 8, and 9, respectively, Co in the  $(\text{Co},\text{Fe})_3\text{V}$  alloy can be replaced by an equal amount of an equiatomic mixture of Ni and Fe, which alters the alloy composition but not  $e/a$ . As long as the electron concentration falls roughly in the same range as  $(\text{Co},\text{Fe})_3\text{V}$ , the ordered cubic structure remains stable in the  $(\text{Ni},\text{Co},\text{Fe})_3\text{V}$  alloys. Eventually, all Co atoms can be replaced by Ni and Fe atoms, leading to the formation of  $\text{L}_{12}$  ordered cubic alloys of the composition  $(\text{Ni},\text{Fe})_3\text{V}$  without any Co elements [20,21].

In addition, control of the ordered crystal structures offers an effective way for tuning the room-temperature ductility of several ordered hexagonal and cubic alloys. Room-temperature tensile elongation of the  $\text{Ni}_3\text{V}$ – $\text{Co}_3\text{V}$ – $\text{Fe}_3\text{V}$  alloys with different crystal structures are presented in Fig. 2 [21]. The hexagonally ordered alloys  $\text{Co}_3\text{V}$  and  $(\text{Ni},\text{Co})_3\text{V}$  are very brittle with less than 2% elongation at room temperature [20,21]. Their low ductility can be attributed inherently to their hexagonal crystal structure, which has limited numbers of slip systems. By contrast, the  $\text{L}_{12}$  ordered cubic alloys with the compositions of  $(\text{Fe},\text{Co})_3\text{V}$ ,  $(\text{Fe},\text{Co},\text{Ni})_3\text{V}$ , and  $(\text{Fe},\text{Ni})_3\text{V}$  are all very ductile, showing a tensile elongation of above 40%. The deformation behavior of these  $\text{L}_{12}$  ordered cubic alloys is similar to that of face-centered cubic (fcc) materials having twelve {111} slip systems. Therefore, the crystal structure of the ordered intermetallics alloys can be altered from hexagonal  $\text{Co}_3\text{V}$  and  $(\text{Ni},\text{Co})_3\text{V}$  to cubic  $(\text{Fe},\text{Co})_3\text{V}$ ,  $(\text{Fe},\text{Co},\text{Ni})_3\text{V}$ , and  $(\text{Fe},\text{Ni})_3\text{V}$  via a macro-alloying approach, which significantly enhances the ductility of the ordered intermetallics. The control of ordered crystal structures and ductility by macro-alloying represents a major advance in alloy design of ductile ordered intermetallics. At the present time, the study of high-entropy alloys (HEAs) with close to equiatomic compositions has

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