Development of Ductile Long-Range Ordered Alloys
For Fusion Reactor Systems*

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Abstract

A series of Fe-base ordered alloys with compositions $(\text{Fe,Ni,Co})_3\text{V}$ are developed for fusion reactor applications. The alloys from cubic ordered structure similar to AuCu_3 below their critical ordering temperature. The alloys in the ordered state are ductile with elongation in excess of 35% at room temperature. Tensile tests of the ordered alloys at elevated temperatures indicate an unusually attractive mechanical behavior. Their strength, instead of decreasing as with conventional alloys, increases with temperature because of ordering effects. As a result, the ordered alloys are much stronger than 316 stainless steel, particularly at elevated temperatures. The ordered alloys are also very resistant to creep deformation. The creep rate of the ordered alloys is lower than that of 316 stainless steel by 3 orders of magnitude at 650°C . A combination of excellent strength and adequate ductility makes the Fe-base ordered alloys unique for high-temperature structural applications.

Introduction

The structural material used for construction of first wall in fusion energy systems is required to possess good high-temperature mechanical properties, resistance to radiation-induced swelling and embrittlement, and good compatibility with low-pressure hydrogen, lithium and coolants.¹ To meet these material requirements, a wide variety of alloys based on Fe, Ni, V, Mo and Nb are being

*Research sponsored by the Division of Advanced Technology Projects, U.S. Department of Energy under Contract W-7405-eng-26 with the Union Carbide Corporation.

studied as possible candidate materials. Current research and development efforts are mainly concentrated on the selection and characterization of conventional alloys such as austenitic stainless steels and commercial super-alloys; however, very little effort is spent on the study of innovative materials such as alloys forming long-range order (LRO) below their critical temperature (T_c).

LRO alloys offer potential advantages over the conventional or disordered alloys for high-temperature structural applications.² This is because kinetic processes involving diffusion, such as creep or migration of point defects, are reduced in the ordered lattice. Also, unusual dislocation motion characteristics of the ordered lattice provides the LRO alloys excellent high-temperature strength and fatigue resistance. Furthermore, some electron irradiation experiments have demonstrated³ that alloys with LRO structure can be more resistant to radiation-induced swelling. This provides incentive to examine the potential of LRO alloys for fusion reactor applications.

One of the main disadvantages that limits the use of LRO alloys has been their tendency to be brittle in the ordered state. However, the recent work of Liu and Inouye⁴ on Co-base ordered alloys with compositions $(\text{Co,Fe,Ni})_3\text{V}$ has overcome the material limitations. They have demonstrated that the ductility of the ordered alloys can be controlled by adjusting the composition and ordered structure. The alloys with controlled ordered structure have more than 30% elongation at room temperature. For fusion reactor applications the Co contents should be limited to <25% because of its high neutron absorption cross section that lowers the tritium breeding rate. In this study, the alloy compositions are modified specifically for fusion reactor applications in the temperature range of 400–700°C.

In the present study, a series of ordered alloys were prepared with a base composition of Fe_3V where Fe is partially replaced with Ni and Co. Ni and Co were added to raise T_c and control the ordered structure. Mechanical properties of the ordered alloys were determined at elevated temperatures and compared with 316 stainless steel, the primary candidate alloy for first-wall construction.

Experimental Procedure

The alloys LRO-15 to 18, with their nominal composition listed in Table 1, were prepared by arc melting or electron-beam melting and drop casting into $25 \times 13 \times 140$ mm rectangular ingots. The ingots were clad in Mo cover sheets and rolled with a total reduction of 80% at 1000–1100°C. After breakdown rolling, the alloy plates were cold rolled from 2.5 to 0.76 mm with an intermediate anneal at 1200°C. The as-rolled sheets were of good quality with no indication of edge or end cracks.

The ordered structures of these alloys were determined by x-ray diffraction, using chromium radiation with a 114.6 mm Debye-Scherrer camera. Chromium radiation was used to obtain maximum superlattice reflection intensities as a result of the anomalous scattering by vanadium atoms.

Sheet specimens with a gage section of $13 \times 12 \times 0.6$ mm were used for tensile and creep tests. Tensile tests were performed at a crosshead speed of 0.25 cm/min. To perform the tensile test at elevated temperatures, a water-cooled quartz-tube vacuum system was attached to the Instron testing machine, and specimens were heated inductively in a Ta susceptor. The load-time curves were used to obtain stress-strain data. Creep tests were done in vacuum under dead-load arrangement. Fracture surfaces of selected specimens were examined with a JSM-U3 scanning electron microscope (SEM) operated at 25 kV.

Table 1. Electron Density (e/a), Ordered Structure and Critical Ordering Temperature (T_c) of AB_3 -Type Ordered Alloys with Compositions $(Fe, Ni, Co)_3V$.

Alloy	Nominal composition	e/a	Ordered structure	$T_c(^{\circ}C)$
LRO-15	$(Fe_{48}Ni_{25}Co_{27})_3V$	7.828	Ordered, α'	760
LRO-17	$(Fe_{52}Ni_{39}Co_{19})_3V$	7.895	Ordered, α'	700
LRO-16	$(Fe_{61}Ni_{29})_3V$	7.835	Ordered, α'	670
LRO-18	Fe_3V	7.250	Disordered (?)	-

Results

The phase relation and ordered structure in these alloys were determined by quenching and aging in the temperature range 300 to 1200°C. The disordered fcc solid solution existing in alloys LRO-15 to 17 at high temperatures, was retained at room temperature on quenching from 1150°C. The α phase decomposes into $\alpha + \sigma$ at temperature below 1100°C. X-ray diffraction indicates that the σ phase has the tetragonal structure with lattice parameter close to those for the σ phase in Fe-V, Co-V and Ni-V alloy systems. At lower temperatures, atomic ordering takes place in alloys 15 to 17 through the peritectoid reaction $\alpha + \sigma \rightarrow \alpha'$. The α' can also be produced by aging the quenched α at temperatures below the ordering temperature. The cubic ordered phase α' is formed on the fcc lattice with ordered structure similar to AuCu_3 ($L1_2$ type). The superlattice lines of α' are clearly visible in these alloys, using Cr radiation. Atomic ordering does not cause a change in microstructure as shown in Fig. 1. Some inclusions are visible, which are probably interstitial compounds containing V.

The ordering temperature (T_c) was determined by aging-quenching treatment and measurement of thermal expansion. A plot of thermal expansion as a function of temperature reveals a discontinuous change around T_c .⁵ The T_c of the alloys LRO-15 to -17 appears to increase with increasing of Ni and Co concentration (Table 1). The alloy 15 has the highest T_c (=760°C) containing a total of 39 at % Co and Ni. So far, ordering reaction is not detected in Fe_3V . We believe that the T_c would be quite low <400°C, if ordering occurs in Fe_3V .

Effect of atomic ordering on the room-temperature tensile properties is shown in Table 2. Atomic ordering has a small effect on the yield strength (σ_y) but causes a significant increase in tensile strength (σ_t). The

Fig. 1. Microstructure of Alloy-17, $(\text{Fe}_{52}\text{Ni}_{38}\text{Co}_{10})_3\text{V}$ in (a) disordered and (b) ordered states. 250x

Table 2. Room-Temperature Tensile Properties of LRO-15, -16 and -17 in Ordered and Disordered States.

Alloy	State	Strength, MPa		Elongation (%)
		Yield	Tensile	
LRO-15	Disordered	394	881	51.1
LRO-15	Ordered	354	1329	54.7
LRO-17	Disordered	305	711	61.6
LRO-17	Ordered	287	1085	50.1
LRO-16	Disordered	393	820	48.0
LRO-16	Ordered	414	1071	35.2

significant increase in σ_t (30–50%) is a result of distinctly high working hardening rate in the ordered state. It is important to note that the alloys are ductile in both disordered and ordered states. The alloys in the ordered state had 35.2–54.7% elongation at room temperature, demonstrating the ductile behavior of the $(\text{Fe,Co,Ni})_3\text{V}$ alloys with cubic ordered structure.

The tensile properties of the ordered alloys at elevated temperatures are shown in Figs. 2 and 3. The striking result in Fig. 2 is that the σ_y of the ordered alloys increases with test temperature rather than decreasing as that of conventional alloys such as 316 stainless steel. The σ_y increases substantially with temperature above 400°C and reaches maximum around T_c . The strength drops sharply above T_c as a result of disordering effect. The ordered alloys are much stronger than 316 stainless steel in the annealed condition. The σ_y of the ordered alloys reaches approximately 450 MPa, which is 4 times that of 316 stainless steel⁶ at 600°C.

In contrast to the σ_y , the σ_t decreases with test temperature as shown in Fig. 3a. The decrease is apparently due to the recovery effect at elevated temperatures. However, the σ_t of the ordered alloys is higher than that of 316 stainless steel by 100–200%. The tensile elongation of the ordered alloys is not sensitive to test temperatures below 600°C. Above that temperature the ductility of LRO-15 decreases with temperature and reaches a minimum around its T_c . As shown in Fig. 3b, the ductility of the ordered alloy is also better than that of 316 stainless steel at temperatures below T_c .

SEM fractographs typical to the ordered alloys at room-temperature and 650°C are shown in Fig. 4. The LRO-15 alloy showed ductile rupture, characterized by dimples, at these temperatures. The dimples are essentially asymmetric, indicating that the final rupture proceeded by shearing.

Fig. 2. Comparison of Yield Strength of the Ordered Alloys LRO-15 and -16 with 316 Stainless Steel at Room and Elevated Temperatures.

ORNL-DWG 78-22419

Fig. 3. Comparison of Tensile Strength and Elongation of the Ordered Alloys LRO-15 and -16 with 316 Stainless Steel at Room and Elevated Temperatures.

Fig. 4. SEM Fractograph of LRO-15 Specimens Fractured at (a) Room Temperature and (b) 650°C; 3000x.

The creep properties of the ordered alloys were determined at 650°C at 276 MPa. The results are presented in Table 3 and compared with 316 stainless steel. The creep rate increases with Fe content which lowers the T_c of the ordered alloys. The minimum creep rate of the ordered alloys is lower than that of the 316 stainless steel⁷ by approximately 3 orders of magnitude. In addition, the ordered alloys did not rupture after 1000 h test. All of these indicate that the Fe-based ordered alloys are much more resistant to creep deformation than 316 stainless steel.

Discussion

Recent work⁴ on Co-base ordered alloys indicates that electron density (e/a) controls ordered structure in $(Fe, Ni, Co)_3V$ alloys. Electron density is defined as the average per atom of the number of electrons outside the inert gas shells. The alloys with $e/a \geq 8$ have hexagonal ordered structure whose unit cell contains 6 to 9 layers. On the other hand, the cubic ordered structure (α') is stable in the alloys with $e/a < 8$. The alloys with multi-layered hexagonal ordered structure have found to be brittle while the alloys with the cubic ordered structure are ductile. The brittleness of the hexagonal ordered structure is attributed to the restricted number of slip systems and the high frictional stress on slip planes. The e/a of the Fe-base ordered alloys is calculated and listed in Table 1. The observation of the cubic ordered structure in these alloys with $e/a < 7.90$ is apparently consistent with the finding in the Co-base ordered alloys.

The Fe-base alloys with cubic ordered structure (α') are ductile with elongation in excess of 35% at room temperature. This provides another example, in addition to the Co-base ordered alloys, that the ductility of ordered alloy can be improved through control of their ordered structure. The Fe-base

Table 3. Comparison of Creep Behavior of Ordered LRO-15 to -17 with 316 Stainless Steel at 650°C and 276 MPa.

Alloy	Minimum creep rate (cm/cm/h)	Rupture life (h)
LRO-15 ^a	2×10^{-6}	<i>c</i>
LRO-17 ^a	4×10^{-6}	<i>c</i>
LRO-16 ^a	9×10^{-6}	<i>c</i>
316 stainless steel ^b	1×10^{-2}	20

^aSpecimens were in ordered and annealed condition.

^bSpecimens were in annealed condition.

^cTest was stopped after 1000 h.

ordered structure also exhibited dimple-type ductile rupture (Fig. 4). All of these indicate that these ordered alloys have plenty ductility to be used as first-wall structural material in fusion reactor systems.

The ordered alloys have very promising high-temperature mechanical properties. As shown in Figs. 2 and 3, the ordered alloys are much stronger than 316 stainless steel at elevated temperatures. The striking feature of the ordered alloys is that their yield strength, instead of decreasing as that of conventional alloys, increases significantly with test temperature and reaches a maximum around T_c . The increase in strength with temperature has been observed in other ordered alloys² with $L1_2$ structure. These observations suggest that the LRO alloys can be best used at elevated temperatures but below T_c . The T_c of the Fe-base ordered alloys we developed has been tailored to be above 650°C, the limited temperature of current design of the first wall.

The Fe-base ordered alloys are extremely resistant to creep deformation. As shown in Table 3, the creep rate of the ordered alloys is lower than that of 316 stainless steel by 3 orders of magnitude. The resistance to creep deformation in LRO alloys is generally attributed to high activation energy and slow diffusion in ordered lattice.²

The study up to date has demonstrated the superior mechanical properties of the Fe-base LRO alloys. Furthermore, Boettner, Stoloff, and Davis⁸ found that formation of LRO significantly improves the fatigue properties in ordered Ni_3Mn and FeCo-V alloys. Schulson et al⁹ recently proposed that ordered lattice enhances vacancy/interstitial recombination and hence reduces void-swelling rate. In agreement with this, neither dislocation loops, dislocation network, nor voids were observed in ordered Zr_3Al (whose ordered structure is the same

as LRO-15 to 17) after an electron irradiation dose of 30 dpa at temperatures 300-500°C. All of these warrants the further characterization of the ordered alloys for fusion reactor applications.

Acknowledgments

The authors gratefully acknowledge H. Inouye, A. C. Schaffhauser, J. H. DeVan and E. E. Bloom concerning alloy development.

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