The Effects of Ni, Mo, Ti, and Si on the Mechanical Properties of a Cr-free Mn Steel (Fe-25Mn-5Al-2C)

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THE EFFECTS OF Ni, Mo, Ti, AND Si ON THE MECHANICAL PROPERTIES OF A Cr-FREE Mn STEEL (Fe-25Mn-5Al-2C)

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ABSTRACT

The FeMnAlC alloys may hold potential as Cr-free replacements for high strategic material iron-base superalloys, but little is known about their intermediate temperature (650 C to 870 C) mechanical properties. The effects of alloying elements on the mechanical properties of model FeMnAlC alloys were studied. Results showed that modified FeMnAlC alloys had promising short term, intermediate temperature properties but had relatively poor stress rupture lives at 172 MPa and 788 C. Room temperature and 788 C tensile strength of FeMnAlC alloys were better than common cast stainless steels. Changes in room temperature tensile and 788 C tensile strength and ductility, and 788 C stress rupture life were correlated with changes in Ni, Mo, Ti, and Si levels due to alloying effects on interstitial carbon levels and carbide morphology. Fe25Mn-5Al-2C had a very poor stress rupture life at 172 MPa and 788 C. Addition of carbide-forming elements improved the stress rupture life.

SUMMARY

As part of NASA's COSAM program, the effects of common alloying elements on the mechanical properties of model FeMnAlC alloys were investigated. Ni, Mo, Ti, and Si were added to Fe-25Mn-5Al-2C. Tensile strength (R.T. and 788 C) and stress rupture life (788 C, 172 MPa) were determined. Tensile and stress rupture properties were found to vary systematically with alloy additions. It was found that Ni and Mo have the strongest influence on mechanical properties, especially on increasing ductility, by changing the distribution of carbon. Both Ti and Si also affect the mechanical properties but to a lesser extent at the concentration levels studied. At room temperature, those alloys with combined additions of Ni and Mo exhibited greater than 10 percent elongation. Fe-20Mn-5Ni-10Mo-5Al-2C had about 15 percent ductility at room temperature. At 788 C, the FeMnMoAlC alloys had a tensile strength of between 276 and 312 MPa and an elongation of between 12 and 38 percent. The FeMnAlC alloys without Mo carbides had a stress rupture life of 0.1 hours at 788 C and 172 Mpa. Those alloying additions which formed carbides (Mo, Si, Ti) had a stress rupture life between 1.35 and 5 hours. Fe-20Mn-5Ni-10Mo-5Al-2C alloys had reasonable tensile strength and ductility at room temperature and 788 C. While FeMnAlC alloys were found to have tensile strengths greater or equal to cast stainless steels, they were found to have poor stress rupture lives at 172 MPa and 788 C.
INTRODUCTION

Iron-base alloys found early application in gas-turbine engines but as nickel-base superalloys were developed, the use of iron-base alloys was greatly reduced. Recently, supply and price instabilities in strategic elements have renewed interest in iron-base alloys for aerospace applications. As part of NASA's program on Conservation of Strategic Aerospace Materials (COSAM), FeMnAlC alloys were evaluated as to their potential for intermediate temperature (650 C-870 C) applications.

FeMnAlC alloys were the subject of many investigations in the 1930's and 1940's and again in the 1960's. They were examined as potential replacements for FeNiCr alloys. The results of the early studies were mixed. In general, alloys in the range of Fe-25-30Mn,5-10Al,0.5-1.5C were found to have tensile properties similar to or greater than 304 and 316 stainless steels at room temperature. Little was published on their intermediate temperature tensile and stress rupture properties.

The face-centered cubic austenite phase has been preferred for improved high temperature mechanical properties in iron-based alloys. In FeMnAlC alloys, Mn is substituted for Ni and Al is substituted for Cr. Chromium is considered to be a strategic metal in the aerospace industry. Although Ni is not on the strategic materials list, manganese could be a low-cost substitute for Ni. Although the United States imports 100 percent of its manganese supply, there are numerous sources for this element. Elemental balance is critical for austenite phase stability in FeMnAlC. Al, Si, and Mo, which are added to iron alloys to confer oxidation resistance (Al,Si) and solid solution strengthening (Mo), stabilize ferrite. Mn, Ni, and C are austenite stabilizers. Mn, however, is only about half as effective an austenite stabilizer as Ni. Also, Mn levels greater than 30 percent promote the formation of a brittle, a Mn structure. Also, unfortunately, large amounts of carbon can be effectively removed from the matrix by carbide formers, thereby reducing the effect of carbon on austenite stability.

This present investigation was undertaken in order to better understand the effects of systematic element variation on the mechanical properties and phase stability of model FeMnAlC alloys.

EXPERIMENTAL

Materials

Seven alloy compositions were chosen for this study as shown in Table I. These compositions were based around Fe-25Mn-5Al-2C. Ni, Mo, Si and Ti concentrations were varied along with the major elements in order to determine the effects of alloy additions. Composition effects were varied in three groups; austenite stabilizers, carbide formers, and oxide formers. Mn and Ni are the principle austenite stabilizers of this group of elements. The Mn content was varied from 25 to 20 percent and the nickel content was varied from 0 to 5 percent as represented by alloys 1, 3, and 7 versus alloys 2, 4, 5, and 6 respectively. Mo was added as a carbide formers and for solid solution strengthening. Its effect may be seen in alloys 3-7 versus alloys 1 and 2. Ti was added as a carbide former as in alloy 5. Finally, the effects of oxide formers (Al, Si) on mechanical properties were determined by the differences in alloys 1-5 versus alloys 6 and 7 in which Si partially replaced Al.
High purity alloying materials were added to 1018 steel during induction melting. 1018 steel has the composition Fe-0.3Mn-0.2Si-0.17C with traces of P, S, Cu, and Cr. Alloys were melted in zirconia crucibles under an argon atmosphere. Alloys were cast into button head tensile bars.

Mechanical Testing

Alloys were tested in the as-cast condition in tension at room temperature and 788 °C and for stress rupture at 788 °C. Standard ASTM E-8 tensile specimens with a gage length of 35mm were tested in tension at a cross head speed of 0.02 mm/s. Stress rupture specimens were tested with a load of 172MPa. Although this stress level is low for disc applications, this load was chosen as a common load level for comparison with previous work.

Microstructural Characterization

The structure and mode of deformation were studied by optical and scanning metallography. For optical microscopy, specimens were conventionally polished then etched with a solution of one part HNO₃, one part HCl, and one part acetic acid. Fracture surfaces were gold coated before observation in the scanning electron microscope. The volume percent ferrite was determined magnetically by a ferrite scope. The volume percent carbide was determined by point counting using a Hilliard 16 point grid.

RESULTS

Microstructure and Constitution of FeMnAlC Alloys

The percent ferrite and carbide phases are shown in Table II. Alloy compositions 1 and 2, where the variables were Mn and Ni, are three-phase alloys composed of austenite, discontinuous carbide, and ferrite phases. FeMnAlC alloys previously had been observed to dissolve large amounts (0.9 percent) of C without precipitating visible carbides. Microstructural examination and x-ray diffraction results indicated that the carbon range can be extended up to 2 weight percent without forming visible carbides. Both compositions, regardless of Ni content, had about 3 percent ferrite. When Mo (or Mo+Ti) was added (alloys 3, 4, and 5), a MgC carbide was developed. This carbide was continuous along dendrite boundaries as shown in Fig. 1(a). In alloys 6 and 7, where Si was substituted for Al, a complex eutectic carbide was formed as shown in Fig. 1(b). Alloys 3-7 had less than 0.2 percent ferrite.

Mechanical Properties

The mechanical properties of alloys 1-10 are given in Table III and Fig. 2-4. Representative microstructures are shown in Fig. 5-10.

Room Temperature Tensile Properties

The tensile strength of Alloys 1-7 varied from 374 MPa to 924 MPa. Of the alloys studied, only alloys 4 and 5 had reasonable ductility at room temperature (Table III). All other alloys had less than 1 percent ductility at room temperature. Therefore, the tensile strengths of the other alloys (1, 2, 3, 6, 7) must be considered as brittle fracture strengths. Alloy 1, the strongest alloy, had 25 percent Mn but no Ni, Mo, Ti, or Si. When 5 percent Ni was added
(alloy 2), the tensile strength was reduced to 603 MPa. When 5 percent Ni was added (alloy 2), the tensile strength was reduced to a lower strength than similar alloys with 20 percent Mn and 5 percent Ni. When 10 percent Mo was added to Fe-25Mn-5Al-2C (alloy 1 + 10 percent Mo = alloy 3), the tensile strength was reduced by about 40 percent with no increase in ductility. In contrast, alloy 4 (alloy 2 + 10 percent Mo) was considerably stronger and more ductile than alloy 2. When 1 percent Ti was added (alloy 5), the room temperature strength and ductility were slightly reduced compared with alloy 4, but this alloy still showed improved properties compared to alloy 2. The addition of silicon (alloys 6 and 7) markedly reduced both the room temperature strength and ductility. In alloy 7, the combination of 25 percent Mn, 10 percent Mo, and 3 percent Si yielded the lowest strength and ductility of the seven alloys evaluated.

The mode of fracture varied as a function of alloy composition. Alloy 1 and 2, which did not contain Mo and were brittle at room temperature, exhibited a transgranular fracture surface as shown in Figure 5(a) (alloy 1). Alloy 2 formed stress-induced martensite near the fracture surface as shown in a cross section, Fig. 6. With the addition of Mo to alloy 1 (alloy 1 + 10 percent Mo = alloy 3), the mode of fracture changed to a mixed intergranular-transgranular fracture as shown in Fig. 5(b). However, this alloy was still brittle at room temperature. With 5 percent Ni added (alloy 4), the fracture surface changed to a ductile platy fracture (as shown in Fig. 5(c)) and the elongation was 15 percent. The addition of 1 percent Ti (alloy 5) did not change the mode of fracture. Alloys 6 and 7 (2.5 percent Al, 3 percent Si), which developed extensive carbides, formed a platy fracture through the matrix and a transgranular fracture across the carbides.

788 C Tensile Properties

The 788 C tensile strength of alloys 1-7 varied from 214 MPa to 345 MPa. Alloy 1 had the highest tensile strength and lowest ductility at 788 C. Alloy 2, where 5 percent Ni replaced 5 percent Mn, had the lowest strength but highest ductility. In alloys 2, 4, and 6, a lower Mn (20 percent) and higher Mn (5 percent) content greatly increased the ductility of the alloys. Alloy 3 (alloy 1 + 10 percent Mo) had a lower tensile strength but higher ductility than alloy 1. In contrast, when Mo was added to alloy 2 (alloy 4), there was an improvement in tensile strength without a loss in ductility. The addition of 1 percent titanium to alloy 4 (alloy 5) lowered the percent elongation by about 55 percent. At 788 C, silicon did not appear to significantly affect either the strength or ductility of alloys 6 or 7 (compared to alloy 4 or 3) at 788 C.

At 788 C, as at room temperature, fracture surface morphology depended on alloy composition. In alloy 1, a band of stress-induced martensite was formed near the fracture surface (as shown in Fig. 7(a)). At the surface, massive platelets were formed. Near the martensite-austenite boundary there was a transition zone where the size and number of platelets decreased. The shape of the boundary was irregular. When 5 percent Mn was replaced by 5 percent Ni, the yield strength was lowered. During testing, the austenitc matrix deformed plastically around the rigid carbide nodules. The carbide nodules developed fractures perpendicular to the principle stress axis as shown in Fig. 7(b).
These large flaws formed the roots of voids as shown in Fig. 8(b). Alloys 3-7, which contained continuous carbides, deformed differently than alloys 1 and 2. These alloys behaved as ductile matrix-brittle fiber composites, as shown in Fig. 9(a). Fracture in these alloys occurred in the carbide phase, as shown in Fig. 9(b). Delamination between the carbide and the austenitic matrix did not occur. Secondary carbide precipitation occurred along slip bands, as shown in Fig. 10.

**Stress Rupture Life**

Alloys 1-7 were loaded at a stress level of 172 MPa at 788 C. This stress level was below the yield stress of all the alloys — except for alloy 2, where the yield stress was nearly equivalent to the applied stress. Unlike tensile strength, which was highly dependent on alloying effects, the stress rupture life was primarily dependent on carbide strengthening. Alloys 1 and 2, without extensive carbides, had extremely low stress rupture lives, about 0.1 hours as shown in Fig. 4. Alloys which contained carbides had stress rupture lives between 1.35 and 5 hours. The microstructures of stress rupture specimens were similar to 788 C tensile specimens.

**DISCUSSION**

The mechanical behavior of model FeMnAlC alloys was strongly influenced by individual and combined alloying effects. These influences may be categorized as:

- Effect of Mn and Ni on matrix properties;
- Effect of interstitial carbon;
- And secondary phase effects.

**Mn/Ni Effects**

The level of Mn and Ni had a strong effect on the tensile properties of FeMnAlC alloys particularly at room temperature. Both Mn and Ni are added primarily as austenite stabilizers. Two parts Mn are equivalent to one part Ni. The as-cast alloys had very low ferrite contents. Alloys 1 and 2 had ferrite contents of about 3 percent while alloys 3-7 had ferrite contents of less than 1 percent. This small difference in ferrite is probably not a valid explanation of the great difference in stress rupture lives between alloys 1 and 2 (~ 0.1 hours) and alloys 3-7 (1.35-5 hours).

Another factor may be due to the strong work-hardening effect of Mn. This effect is believed due to the effect of Mn on stacking fault energy. The effect of alloying on stacking fault energy in austenitic stainless steel has been studied by Schramm and Reed. They found that Ni has a strong positive contribution to the stacking fault energy while Mn has only a slightly positive contribution (Ni = 2 Mn). Wide splitting of partial dislocations (as reflected in a low SFE) in high Mn steels leads to barriers to dislocation motion.

The high tensile strength and low ductility of alloy 1 at 788 C can be contrasted with the low tensile strength and high ductility of alloy 2. In these alloys, the level of Mn and Ni was the only composition difference. This pattern of low ductility in the 25 percent Mn alloys (3 and 7) versus high ductility in the 20Mn-5Ni alloys (4, 5, 6) is consistent at 788 C. However, the level of Mn and Ni did not affect the stress rupture life. Although alloys 1 and 2 differed in Mn and Ni, they had stress rupture lives of 0.1 hours.

Alloys 3-7, which varied in Mn and Ni concentration, had similar stress rupture lives. It is also unlikely that differences in stress rupture lives may be explained by the small difference in percent ferrite (3 percent vs <1 percent).
Interstitial solute atom concentration has a significant influence on the strength and ductility of FeMnAlC. Molybdenum, through the formation of carbides, effectively lowers the interstitial concentration of carbon in FeMnAlC. While alloys 2 and 4 differ only in Mo content, alloy 4 (10 percent Mo) is significantly stronger and more ductile than alloy 2 (0 percent Mo). This improvement in mechanical properties is believed to be due to Mo removing carbon from interstitial sites to form carbides.

Secondary Phase Effects

Carbide phases are perhaps the primary factor in determining the strength of FeMnAlC. In alloys 3-7, extensive carbides (30-56 percent) form prominent barriers to the movement of dislocations. In these alloys, fracture occurs within the carbide phase rather than in the austenite or by delamination between the matrix and carbide phases. Since carbides in alloys 3-7 are continuous, they form an easy crack path. Therefore, the strength of these alloys, particularly at room temperature, is governed by the strength and distribution of carbides. This can be observed in the differences between alloys 4 and 5 and alloys 6 and 7. When silicon is added, as in alloys 6 and 7, the volume fraction of carbides is increased leading to a reduction in room temperature strength. At 788°C, this does not appear to be as significant in short term tensile testing. Carbides appear to improve the stress rupture life of these alloys. Alloys 1 and 2 had a stress rupture life of 0.1 hours. When continuous carbides were formed, the stress rupture life improved to between 1.35 and 5 hours. The increase in stress rupture life appeared to be independent of carbide morphology.

SUMMARY OF RESULTS

The effects of alloying element on the mechanical properties of model FeMnAlC were studied. It was determined that Fe-20Mn-5Ni-10Mo-5Al-2C had promising room temperature and 788°C tensile strength and ductility. The FeMnAlC alloys had tensile strengths greater than or equal to conventional cast stainless steels as shown in Figure 11. However, the stress rupture lives of FeMnAlC alloys are poor at 172 MPa and 788°C. The effects of alloying additions may be summarized as:

1. Ni and Mo have the strongest influence on mechanical properties, especially by increasing ductility. Mo influences the ductility by changing the distribution of carbon.
2. While Ni additions alone lower the room temperature strength without an improvement in ductility, Ni + Mo additions result in greater strength and ductility than Mo additions alone. The addition of Ni increases the mechanical stability of austenite at room temperature.
3. Carbides, formed by the addition of Mo, improve the stress rupture life of FeMnAlC. The presence of carbides resulted in a ten-fold increase in stress rupture life.
4. The addition of 1 percent Ti improved the 788°C rupture life and tensile strength with a slight loss in ductility. The room temperature strength was slightly decreased.
5. Substituting silicon for part of the Al significantly reduced room temperature tensile properties, but had little effect on the stress rupture and tensile strength at 788°C.

Fe-20Mn-5Ni-10Mo-5Al-2C shows promise for continued study due to combined room temperature and 788°C tensile strength. The mechanisms of long term failure require further study before FeMnAlC alloys can be considered for aerospace applications.

REFERENCES

TABLE I. - COMPOSITION OF MODEL FeNiMoAl TiC ALLOYS

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<th>Alloy</th>
<th>Nominal Composition, wt. %</th>
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TABLE II. - PHASES PRESENT IN MODEL FEMNAlC ALLOYS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal Composition, wt. %</th>
<th>Percent Ferrite</th>
<th>Carbide Phases</th>
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Mn = Fe, Mn.
Mo = Mo, Fe.
CM = Fe, Mo, Ti.
GM = Fe, Mo, Ti, Si.
### TABLE III. - MECHANICAL PROPERTIES OF Fe-Mn-Al-C ALLOYS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal Composition, wt. %</th>
<th>Room temperature (MPa)</th>
<th>788 C (MPa)</th>
<th>Stress rupture (788°C/172 MPa) life, hr</th>
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<tr>
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<td>UTS  YS    Percent Elongation</td>
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</table>
(a) Fe₂₀M₅Ni₅Si₁₀M₂C₃
(b) Fe₂₀M₅Ni₂₅Si₁₀M₂C₃

Figure 1. A comparison of Mo and Si additions on carbide morphology in FeMnAlC.

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Figure 2. Comparison of ultimate tensile strengths of modified composition FeMnAlC alloys.
Figure 3. Comparison of percent elongation of modified composition Fe-Mn-Al-C alloys.

Figure 4. Effect of carbide morphology on 788C/172 MPa stress rupture life.
Figure 5. - SEM fractographs of room temperature tensile specimens showing (a) transgranular (b) transgranular-intergranular, and (c) ductile platy fracture.

Figure 6. - Stress-induced martensite formation during tensile test at room temperature.
Figure 7. Effect of Ni on the 788°C deformation of Fe-Mn-Al-C.

Figure 8. Mode of fracture in Fe20Mn5Ni5Al2C (alloy 2) at 788°C.
Figure 9. - Fracture cross section of Fe20Mn5Ni5AI10Mo2C (alloy 4).

Figure 10. - Photomicrograph of carbide precipitation on slip bands in Fe20Mn5Ni5AI10Mo2C.
Figure 11. Elevated temperature tensile strength of commercial cast stainless steel vs NASA FeMnAIC alloys.