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**HIGH-TEMPERATURE MICROSTRUCTURAL STABILITY
IN IRON- AND NICKEL-BASE ALLOYS FROM RAPID
SOLIDIFICATION PROCESSING**

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ABSTRACT

A series of iron- and nickel-base alloys was processed by several atomization methods, consolidated into monolithic forms, and heat treated under various conditions, including very high temperature, isothermal exposures. After heat treatment, the microstructure and microstructural stability were examined and mechanical property testing was performed. The results from the microstructural examinations are summarized and correlated with those from the mechanical properties tests.

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INTRODUCTION

The properties and performance of metallic alloys for heat resistant applications depend on the fineness, homogeneity, and stability of their microstructures, particularly after high temperature exposures. Potential advantages of rapid solidification processing (RSP) of alloys for such applications are the homogeneity in composition and fine microstructural features derived from the nature of the RSP process. The main RSP product form is powder, which is obtained by atomizing a narrow melt stream into fine molten droplets. Rapid cooling of the droplets is typically achieved through convective cooling with noble gases such as argon or helium.

Consolidation of RSP powder, either using near-net-shape methods or into forms that can be converted to final product shapes, requires exposures to fairly high temperatures, usually 900 to 1200°C for iron- and nickel-base alloys. Full consolidation, i.e., complete densification with accompanying particle bonding, usually requires pressure or stress assistance. Consolidation, as well as any subsequent thermal-mechanical processing, may affect the chemical homogeneity and fine microstructures.

A study has been performed on a series of RSP iron- and nickel-base alloys. The results of microstructure examinations and mechanical properties tests of the consolidated powders, and their correlation, will be covered in this paper.

MATERIALS

The iron-base alloys investigated were primarily stainless steels. Rather complete microstructural evaluations have been performed on Type 304 SS and on an experimental alloy, Fe-16Ni-9Cr-1.5Mn-0.04C. Less extensive evaluations have been made for several other iron-base alloys. The primary nickel-base alloy investigated was the superalloy 718. A Ni-20Fe-20Cr alloy series with different carbon levels has also been examined.

PROCESSING

Powders were prepared by three atomization methods, centrifugal (CA), inert gas (IGA), and vacuum gas (VGA). The IGA and CA methods are shown schematically in Fig. 1. The VGA process is similar to the IGA method, but the system is inverted and the gas in the chamber for convective cooling is at a lower pressure.

It is difficult to determine the ranges of the cooling rates for these atomization methods. The solidification rate can be estimated from the fineness and the morphological features of the microstructures of the powder particles. CA and IGA appear to have comparable solidification rates that are significantly higher than the rate for the VGA method (1,2). Boundary spacings for Type 304 SS powders prepared by these three methods are shown in Fig. 2. The VGA powder had a cellular microstructure, the CA and IGA were dendritic. It is apparent from Fig. 2 that the fineness of the microstructure is a function of particle size.

The primary consolidation methods used were extrusion and hot isostatic pressing (HIPping). Most of the iron-base alloys were consolidated at 900°C. The exceptions are Fe-20Ni-20Cr and Ni-20Fe-20Cr with and without 2Mo, each with three carbon levels, which were HIPped at 1100°C. An 1100°C preheat was

Fig. 1. Schematics of inert gas atomization (left) and centrifugal atomization (right) for powder processing.

Fig. 2. Influence of particle size on the boundary spacings (microstructure fineness) for VGA, CA, and IGA processed Type 304 SS powders.

used for extrusion consolidation of the Alloy 718 powder. Dynamic consolidation with explosives, a relatively low bulk temperature method, was used on some of the Type 304 SS powder (3,4). The consolidated powders (i.e., bar or plate) were subjected to a variety of heat treatments, mainly isothermal anneals to high temperatures. For alloys where precipitation strengthening is important, i.e., superalloys A286 and 718, aging treatments were also performed. Grain sizes were determined for longitudinal cross sections by the linear intercept method after annealing. The submicron microstructural features were determined via TEM/STEM.

MICROSTRUCTURE

GRAIN SIZE - All of the consolidated iron- and nickel-base alloys investigated had fine grain sizes and showed resistance to grain growth at temperatures up to 1200°C. Extensive grain growth was observed at much lower temperatures in the conventionally processed counterparts (CPCs) prepared by ingot metallurgy (I/M). The influence of powder processing and consolidation parameters on the grain size behavior is presented in Fig. 3 for Type 304 SS. It is apparent that the grain size/growth behavior is largely independent of powder atomization method (Fig. 3a), consolidation method (Fig. 3b), and particle size (Fig. 3c) for RSP Type 304 SS. The influence of particle size on oxide film and dendrite arm spacing in the IGA alloy are also included in Fig. 3c. These powder characteristics had no effect on the grain size.

The grain sizes of the consolidated powders and their CPCs after a 1 h-1100°C anneal are shown in Table 1. All of the RSP alloys have substantially smaller grain sizes than their CPCs. The differences in grain size among the RSP alloys were relatively small, suggesting that alloy composition is not a major factor in the grain growth behavior. It is interesting to note that in the two alloy series involving different carbon levels, Fe-20Ni-20Cr with and without 2% Mo and Ni-20Fe-20Cr with and without 2% Mo, the CPC alloys show an apparent strong dependence of grain size on carbon content while the CA alloys show only a modest dependence on the carbon level.

The relative insensitivity of the RSP alloys to processing (atomization and consolidation method) and alloy composition is surprising. Based on this information, it is reasonable to assume that the mechanism for retention of the fine grain sizes in the atomized powder products is the same for all of the alloys evaluated in this study. This mechanism has not been conclusively resolved yet, but is addressed further in the following section.

SUBMICRON MICROSTRUCTURAL FEATURES - TEM/STEM examinations were performed on most of the consolidated alloy powders listed in Table 1. However, only

Fig. 3. Influence of processing parameters after 1 h heat treatments on grain size for consolidated Type 304 SS powders: (a) powder processing, (b) powder consolidation, and (c) powder particle size effects.

Fig. 3. (Continued)

two alloys, Type 304 SS (CA, IGA, and CPC) and Fe-16Ni-9Cr (VGA and CPC), have undergone extensive examinations.

The submicron microstructural features of the CA and IGA Type 304 SS extruded powders show evidence of stability after high temperature heat treatments compared to the CPC materials. Their high, and stable, dislocation densities are shown in Fig. 4. It is apparent that the powder atomization processes have introduced some type of defect that is pinning the dislocations. Fig. 4 also shows that for the IGA material destabilization (i.e., unpinning) of the dislocations occurred between 1200 and 1300°C.

Table 1 - Grain Size for RSP Consolidated Iron- and Nickel-base Alloy Powders and CPCs After 1 h-1100°C Heat Treatment

Alloy	RSP and Consolidation Methods	Grain Size (mm)		Alloy ^a	Grain Size (mm)	
		RSP	CPC		RSP	CPC
304	CA, Extrusion	0.014	0.184	Fe-20Ni-20Cr-0.005C	0.014	0.133
	VGA, HIP	0.016	--	Fe-20Ni-20Cr-0.04C	0.013	0.058
	IGA, Extrusion	0.008	0.150	Fe-20Ni-20Cr-0.14C	0.010	0.036
430	IGA, Extrusion	0.024	0.148	Fe-20Ni-20Cr-2Mo-0.004C	0.016	0.140
PH 13-8(Mo)	IGA, Extrusion	0.010	0.055	Fe-20Ni-20Cr-2Mo-0.06C	0.013	0.054
				Fe-20Ni-20Cr-2Mo-0.15C	0.010	0.038
A286	IGA, Extrusion	0.008	0.124	Ni-20Fe-20Cr-0.008C	0.016	0.146
718	IGA, Extrusion	0.011	0.130	Ni-20Fe-20Cr-0.04C	0.012	0.052
				Ni-20Fe-20Cr-0.14C	0.013	0.035
Fe-16Ni-9Cr-0.04C	VGA, Extrusion	0.019	0.216	Ni-20Fe-20Cr-2Mo-0.006C	0.012	0.126
	VGA, HIP + CW	0.017	0.216	Ni-20Fe-20Cr-2Mo-0.03C	0.010	0.057
	IGA, Extrusion	0.018	0.200	Ni-20Fe-20Cr-2Mo-0.14C	0.011	0.021
Fe-16Ni-9Cr-5Mo-2Cu-0.05C	VGA, Extrusion	0.012	0.105			

a. Alloys in this column are all CA, HIP + CW.

Fig. 4. Influence of 1 h heat treatments on dislocation density determinations for CA and IGA Type 304 SS consolidated powders with CPC comparison.

Fig. 5. shows the precipitate behavior of Type 304 SS. The precipitate observed for the CPC material was an $M_{23}C_6$ carbide that dissolved after the 1 h-1100°C heat treatment. At lower temperatures, the carbides were several microns in size and primarily located on grain boundaries. For the two RSP extruded powders, the precipitates were primarily located in the grain interiors, and their average sizes were less than 100 nm at temperatures up to 1200°C. The composition of the RSP alloy precipitates is still under investigation; however, at the lower temperatures (900 and 1000°C) they apparently are primarily chromium carbides. At higher temperatures (1100 to 1300°C), oxygen appears to be present, suggesting that the precipitates are oxides or possibly carbo-oxides. It is interesting to note that the volume fraction of precipitates after the 1 h-1100°C heat treatment is nearly an order of magnitude higher for the CA extruded powder than the IGA material. A high population of near monosized, 8 nm diameter cavities was observed in the CA Type 304 SS extruded powder, but not observed in the IGA Type 304 SS

Fig. 5. Influence of 1 h heat treatments on precipitate behavior for CA and IGA Type 304 SS extruded powders.

material or the other alloys investigated (5-7). X-ray and TEM analysis of the cavities have shown that they are hollow oxides (5-7). Their presence suggests that during crystallization of the molten droplets a supersaturation of vacancies has been trapped in the particles. The cavities/hollow oxides retain their size stability over the temperature range of 900 to 1200°C. These hollow oxides are very effective nucleation sites for the precipitates (7), as shown in representative TEM photomicrographs in Fig. 6. The dispersion resulting from this defect complex lies along dislocations and appears to be relatively uniform in size and spacing, see Fig. 6a. In Figs. 6b and c, through-focal, bright-field imaging reveals the presence of the 8 nm hollow oxides inside of the precipitates.

The precipitate behavior of the VGA Fe-16Ni-9Cr extruded powder is similar to that of the IGA Type 304 SS extruded powder. However, unlike the IGA, CA, and CPC Type 304 SS series shown in Fig. 4, the residual dislocation densities of the VGA material were only a factor of 2 to 3 higher than those of its CPC. The VGA alloy showed no evidence of nanometer sized cavities/hollow oxides.

High temperature stability of the submicron microstructural features and of the grain size is a beneficial aspect of powder atomization processing that needs to be promoted. Although the reasons for this microstructural stabilization have not been resolved, it appears that oxygen may be playing a very important role. The clearest evidence of this is the 8 nm hollow oxides in the CA Type 304 SS extruded powder shown earlier. Small voids formed by vacancy coalescence can be stabilized with a partial coating of dissociated oxygen (8,9). Oxygen significantly lowers the surface energy of a void, making it the most stable vacancy configuration in metals such as Type 316 SS (8,9). The oxygen associated with the void does not remain dissociated, but quickly combines with suitable metal species to form an oxide film around the vacancy cluster. Destabilization of the coated void would be expected to occur at high temperatures where dissolution occurs, i.e., where the thermal energy is sufficient to promote oxide dissolution, or under conditions in which the oxide film can be reduced, e.g., presence of carbon.

Fig. 6. CA Type 304 SS extruded powder after 1200°C-1 h, water quench, and aging for 1000 h at 600°C: (a) overview of cavity-carbide-dislocation morphology, (b) underfocus, and (c) overfocus bright-field image of details of cavity-carbide-dislocation interactions.

The role of oxygen in stabilizing dislocations is not clear. It is possible that a large population of stable oxygen-vacancy defects that are below standard TEM resolution is pinning the dislocations in the CA and IGA Type 304 SS. This could explain the retention of the high dislocation densities shown in Fig. 4.

There are several possible mechanisms for the role of oxygen in promoting and retaining small grain sizes. Two general categories are stabilization and pinning. Oxygen at the grain boundaries could significantly lower the grain boundary surface energy, hence stabilization. Also, a large number of very small (i.e., below standard TEM resolution) oxygen or even oxygen-vacancy dispersions could prove effective for pinning the grain boundaries. The behavior of the precipitates revealed by standard TEM examination (see Fig. 5) does not appear to be responsible for the grain growth retardation observed for RSP alloys investigated in this study. For example, an increase in the volume fraction of dispersions would be expected to increase grain boundary pinning influences. The difference in volume fraction of the precipitates at 1100°C for the CA and IGA Type 304 SS specimens (see Fig. 5) would suggest a substantially stronger influence on grain size in the CA material. Yet, as noted in Fig. 2 and Table 1, the two materials have comparable grain sizes. These precipitates appear to change from carbides to oxides as the temperature increases, implying that there is a source of oxygen in the alloys. Possible sources could be grain boundaries or dislocations that release oxygen when destabilization occurs. The factor of three increase in grain size for both the CA and IGA Type 304 SS after the 1 h-1200°C vs. the 1 h-1100°C heat treatment (see Fig. 3c) supports this argument.

MICROSTRUCTURE CORRELATIONS WITH MECHANICAL PROPERTIES

The RSP iron- and nickel-base alloys show significant increases in tensile strength accompanied by only modest reductions in ductility as compared to their CPCs. Some representative tensile curves are shown in Fig. 7 for Type 304 SS and Fe-16Ni-9Cr-1.5Mn-0.05C at various test temperatures. The influence of grain size on room temperature yield stress for these two alloys is shown in Fig. 8. These results show that a considerable portion of the strengthening observed for the RSP alloys is due to their retention of fine grain size after high temperature heat treatments. As shown in these figures, the grain size dependence is represented by the Hall-Petch correlation (10,11). The yield stress lines of the RSP alloys have significantly different slopes than those of the CPCs (Fig. 8).

An analysis of the matrix stress and its correlation with submicron microstructural features has been performed for the CA Type 304 SS and its CPC (12). Of particular interest are the CA specimens heat treated at 1200 and 1300°C (see Fig. 8a) because they have equivalent grain sizes (~0.03 mm) but significantly different submicron microstructural characteristics. The feature that best explains the increase in matrix stress for the RSP Type 304 SS is the relatively high residual dislocation density (12).

The mechanism responsible for the increased matrix stress in the VGA Fe-16Ni-9Cr-1.5Mn-0.05C alloy has not been resolved. It is possible that the increase is associated with residual oxygen, which was higher for this alloy than for the other alloys investigated.

Both CA Type 304 SS and VGA Fe-16Ni-9Cr-1.5Mn-0.05C have significantly lower slopes for their yield stress lines than do their CPCs, as shown in Fig. 8. There is evidence suggesting that carbon, if present on the grain boundaries, will cause an increase in the Hall-Petch slope (13). For the two RSP alloys, a significant portion of the carbon appears to be associated with matrix precipitates, such as those shown in Fig. 5, and hence less carbon would be expected for segregation at the grain boundaries than in their CPCs.

Fig. 7. Engineering stress-strain curves for various test temperatures: (a) CA and CPC Type 304 SS and (b) VGA and CPC Fe-16Ni-9Cr.

Fig. 8. Influence of grain size on room temperature yield stress: (a) CA extruded powder and CPC for Type 304 SS and (b) VGA extruded powder and CPC for Fe-16Ni-9Cr-1.5Mn-0.05C.

Another example of tensile strengthening is shown in Fig. 9, which presents yield and ultimate stress data for IGA nickel-base Alloy 718 (14). These results show no influence of powder particle size on the room temperature yield and ultimate tensile stresses. The Alloy 718 tensile specimens were given a 1 h-1100°C and water-quench heat treatment, and some received a duplex aging treatment (4 h at 750°C and 16 h at 650°C). The 1100°C anneal produced a grain size of 0.011 mm for the IGA processed powder (independent of the

Fig. 8. (Continued).

particle size used in extrusion) and 0.130 mm for the CPC materials. The difference in yield stresses for the RSP and CPC materials in both unaged and aged conditions is about 150 MPa; i.e., aging did not affect the difference. The increase in yield stress is attributed to the fine grain size for the IGA Alloy 718 extruded powder (14).

Creep appears to be strongly influenced by RSP for the iron- and nickel-base alloys. Typical creep curves for CA, IGA, and CPC Type 304 SS materials

Fig. 9. Influence of powder particle size on the yield and ultimate stresses for extruded Alloy 718 powders before and after a duplex aging treatment.

are given in Fig. 10. These specimens were given an 1100°C-1 h heat treatment prior to testing at 600°C and a stress of 195 MPa. The results show a substantial increase in creep resistance for the CA Type 304 SS compared to both the IGA and CPC materials. The difference between the CA and IGA materials is their precipitate morphology. The CA Type 304 SS, as shown earlier (Fig. 6), contains a large population of nanometer size hollow oxides that provide effective nucleation sites for carbides. This precipitate morphology is not found in the IGA Type 304 SS. The creep curves indicate that the CA Type 304 SS benefits from matrix strengthening, and that grain boundary sliding due to small grain size is not a factor. It should be noted that many of the alloys tested do not show the improvements in creep resistance observed for the extruded CA Type 304 SS, neither was there any evidence of the nanometer-sized hollow oxides and associated matrix precipitates for those alloys examined.

Fig. 10. Creep curves at 600°C and 195 MPa for CA and IGA Type 304 SS extruded powders and CPC.

CONCLUSIONS

The microstructure and mechanical properties of nearly 20 RSP iron- and nickel-base alloys, prepared by several powder atomization and consolidation processes with various heat treatments, were evaluated. Comparisons of the RSP alloys with their conventionally processed counterparts show that the RSP alloys retain fine microstructural features even after high temperature exposures. A consistent feature for all the RSP alloys investigated is a stable fine grain size, which is not significantly influenced by the atomization method used to produce the powder, the consolidation method, or by powder particle size. Submicron microstructural features are significantly affected by the atomization method. One feature unique to centrifugally atomized Type 304 SS extruded powder is the presence of a large population of stable 8 nm size, hollow oxides. These oxides reside along dislocations and provide an effective nucleation site for carbides. The fine grain sizes observed for the alloys provide significant increases in yield stresses. There was no evidence that the fine grain size detrimentally influences the creep behavior of these alloys; however, the CA Type 304 SS extruded powder containing the nanometer-sized hollow oxide-carbide dispersion shows a substantial improvement in creep resistance.

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