NOTICE

**CERTAIN DATA
CONTAINED IN THIS
DOCUMENT MAY BE
DIFFICULT TO READ
IN MICROFICHE
PRODUCTS.**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PROCESSING OF TWO IRON-CHROMIUM OXIDE
DISPERSION STRENGTHENED STEELS BY
MECHANICAL ALLOYING

D. S. GELLES

April, 1989

To be used for
inclusion in Fusion Semi-Annual Report
published by the U. S. Department of Energy

Work Supported by
the U. S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PROCESSING OF TWO IRON-CHROMIUM OXIDE DISPERSION STRENGTHENED STEELS BY MECHANICAL ALLOYING - M. G. McKimpson, A. N. Niemi (Michigan Technology Institute), and D. S. Gelles (Pacific Northwest Laboratory)

OBJECTIVE

The objective of this effort is to determine if oxide dispersion strengthened (ODS) alloys produced by mechanical alloying are suitable for first wall applications.

SUMMARY

Two low activation ferritic ODS alloys have been manufactured, using mechanical alloying procedures, into extruded bar. The alloy compositions in weight percent are: Fe-14Cr-1.0Ti-0.5W-0.25Y₂O₃ and Fe-9Cr-2.0W-0.3V-0.08C-0.25Y₂O₃. Dispersoid phase instability is indicated in the 9Cr carbon-containing alloy, but the 14Cr alloy appears to offer a novel material which may be suitable for first wall applications and warrants further study.

PROGRESS AND STATUS

Introduction

An ODS alloy made by mechanical alloying methods is receiving continued international consideration for liquid metal, fast breeder reactor fuel cladding applications.¹ The alloy shows excellent long term microstructural stability in irradiation environments and is expected to retain superb high temperature strength. The alloy, called MA957, has the composition Fe-14Cr-1Ti-0.25Mo-0.25Y₂O₃ and is made by a powder metallurgy process involving high energy ball milling. The resultant microstructure consists of a metal matrix with a uniformly distributed yttria dispersoid on the order of 5 nm in diameter. It also contains a highly elongated subgrain structure which is introduced by thermo-mechanical processing. Based on performance demonstrated to date, this technology should be considered for fusion first wall applications.

Therefore, an effort has been initiated to consider the use of mechanically alloyed ODS alloys for fusion by altering the alloy composition to be in line with low activation criteria. However, the manufacturer of MA957, the INCOMAP division of the International Nickel Company (INCO), Huntington, W. Va., was unwilling to manufacture a low activation variant, and therefore, a request was made and a responding proposal was submitted by The Institute of Materials Processing (IMP), Michigan Technology University (MTU) to produce two extrusions from mechanically alloyed powder. As accepted, the agreement called for the production of extrusions from mechanically alloyed powder of the following compositions (in weight percent): Fe-14Cr-1.0Ti-0.5W-0.25Y₂O₃ and Fe-9Cr-2.0W-0.3V-0.08C-0.25Y₂O₃. The alloy compositions and method of processing were defined by Pacific Northwest Laboratory (PNL) so that the 14Cr alloy was a low activation variant of MA957 and the 9Cr alloy was a mechanically alloyed version of GA3X, with the development of appropriate process parameters by IMP on a best effort basis. The extrusions were to be supplied to PNL with a 19-mm (3/4-in.) diameter and a minimum 410-mm (16-in.)

length. This report describes the manufacturing process used to produce the requested materials based on the IMP Project No. R-419 report, and provides some preliminary measurements on the products.

Experimental procedure

The starting powder compositions and the maximum mesh sizes are shown in Table 1. Master alloy powders were used, where possible, in an attempt to minimize inhomogeneity in the final product. A 1S Szegvari attritor with a tank capacity of 9.5 L (2.5 gal.) was used for the mechanical alloying. The tank was charged with 27.3 kg (60 lb) of 9.53-mm (3/8-in.) 440C stainless steel balls and 1.82 kg (4 lb) of powder. Two batches of each composition were required. The attritor was operated at 350 rpm with a positive pressure, high purity argon purge rate of 5 L/min. Each batch was attrited for 12 h, held overnight under A, and attrited for 8 h the next day. During attrition, the drive torque and tank lid temperature were monitored. The torque ran between 556 and 570 N-m (410 - 420 in.-lb) and the lid temperature ran between 363 and 380K. The tank and discharge valve were wiped clean after each batch and the powder was screened to -100 mesh to remove any large chunks (there were roughly 16 g of +100 mesh per batch). A sample of powder from each alloy composition was mounted, polished, and examined metallographically to establish that sufficient alloying had been achieved. As shown in the photomicrographs in Figure 1, the powder particles appear to be quite homogeneous. Although not shown in Figure 1, a few powder particles were observed which had not been completely alloyed. Nevertheless, the attrition time was limited to 20 h in order to prevent caking of powder on the walls and bottom of the attritor. Once this problem develops, the powder continues to accumulate until it causes a motor stall or a fracture of some of the stirring components.

Table 1. Compositions and maximum mesh sizes of starting powders

Powder	Composition	Mesh Size
Fe	99.5%	-100
Fe-Cr	74%Fe, 26%Cr	-200
Fe-Ti	60%Fe, 40%Ti	-100
W	99.9%	6 μ m
V-Cr	75%V, 25%Cr	-100
Y ₂ O ₃	99.9%	40 nm

After screening, the two batches of each composition were combined in a v-cone blender for 15 min before consolidation. An attempt was made to cold isostatically press the powder at 400 MPa but did not result in sufficient green strength for handling. Hence, the hot isostatic press (HIP) consolidation was carried out on loose powder. The HIP parameters and can material were determined from trial runs using mild steel or copper tubing

for HIP cans. It was found that densities greater than 98% of theoretical could be achieved using the copper tubing at 1223K for 30 min at 200 MPa. Copper was also chosen for the extrusion billet HIP cans because the steel cans were too rigid to obtain full densification during trial runs using iron powder. The extrusion billets were given a second, higher temperature HIP treatment after removal of the copper can to help ensure full densification. This was done because of a concern about scaling the HIP parameters from copper tubing to the larger size of the extrusion billets. Powder for the extrusion billets was poured through the evacuation stem of a 80-mm diameter x 100-mm length copper can with intermittent vibration to ensure a maximum packing density. After filling, the cans were evacuated and heated under vacuum to 673K where they were maintained for 16 h before sealing the evacuation tubes. Following evacuation and canning, the billets were HIPed at 1223K for 2 h at 200 MPa. After removal of the copper can, the billets were HIPed again at 1373K for 1 h at 200 MPa. They were then machined to dimension (63.5-mm diameter x 66 mm long) for extrusion. A calculation of the bulk density from the machined dimensions showed the billets to be 98% dense, assuming theoretical densities of 7.73 g/cc and 7.90 g/cc for the Fe-14Cr and Fe-9Cr alloys, respectively.

After soaking at 1422K for 2.25 h the billets were extruded at RMI Company of Ashtabula, Ohio. They were given a glass coating as a die lubricant and extruded to 19 mm in diameter with a ram speed of ~1.27 m/min. The maximum ram pressure was 20.7 MPa for both alloys. After extrusion, the Fe-14Cr alloy had severe surface cracks over one-third of its length and the Fe-9Cr alloy had cracks over one-half its length. Figure 5 shows examples of each side of each of these bars. The alloys were shipped to PNL in the as-extruded condition with a recommendation that they be homogenized for 20 h at 1273K. Table 2 shows the results of chemical analyses on samples of the extruded bars.

Table 2. Results of chemical analyses on as-extruded bar

Element	Fe-14Cr		Fe-9Cr	
	Measured	Stated	Measured	Stated
Cr	13.8	14.0	9.10	9.0
W	0.73	0.5	2.01	2.0
V	----	0	0.30	0.3
Ti	0.62	1.0	0.0	---
C	0.051	0	0.096	0.08
Y	0.23	0.20	0.23	0.20

Discussion

The density, hardness, and microstructure of the alloys were monitored during the consolidation, extrusion, and homogenization processes. Initial characterizations were done on test coupons HIPed separately from the extrusion billets. The reason for this was simply that there was not enough room in the HIP chamber for both an extrusion billet and a coupon. Figure 2 compares the microstructure of the two alloy coupons after the first and second HIP treatments. The most notable features are some second phase particles that have been identified by energy dispersive x-ray analysis as Fe-, Cr-, Ti-, V-, and W- rich regions. They are most likely remnant precursor powder particles which escaped the mechanical alloying process. The distribution of these particles is better shown at lower magnification in Figures 3a and 3b. The Fe-, Cr-, Ti-, V-, and W- rich particles (identified in Figure 3a by chemical symbols) seem to appear in relative numbers proportional to the amount of master alloy added to the powder blend. Figure 3b shows the coupon microstructure after homogenization. Note that the particles have almost entirely disappeared. Figure 4 is a comparison of the extrusions before and after homogenizing 20 h at 1273K. Before homogenization, a few precursor particles remain with a fine dispersion of porosity. After homogenization, the porosity becomes very prominent. Table 3 summarizes the hardness and density data for the various stages of consolidation, extrusion, and homogenization. Note that the density of the 14Cr coupon remains nearly constant from the first HIP treatment through the homogenization. The density of the billet increases slightly after extrusion. The density of the 9Cr coupon, however, decreases with each successive high temperature exposure. Although the 9Cr density increases on extrusion, it drops to its original value after homogenization. Also, the hardness of both alloys decreases after each high temperature excursion with the most dramatic drop occurring in the 9Cr extrusion after homogenization. This sudden drop might be at least partly due to the changes in pore size and content, as discussed.

Table 3. Summary of hardness and density data for the various stages of consolidation, extrusion, and homogenization

Condition	Alloy	Density (g/cc)	Hardness (R _C)
HIPed Coupon	14Cr	7.65	48.5
ReHIPed Coupon	14Cr	7.64	39.5
Homogenized Coupon	14Cr	7.64	37.9
HIPed Coupon	9Cr	7.80	49.4
ReHIPed Coupon	9Cr	7.76	42.2
Homogenized Coupon	9Cr	7.74	30.3
ReHIPed Billet	14Cr	7.61	----
Extrusion	14Cr	7.67	37.5
Homogenized Ext.	14Cr	7.66	36.3
ReHIPed Billet	9Cr	7.71	----
Extrusion	9Cr	7.79	32.9
Homogenized Ext.	9Cr	7.71	20.3

In order to better understand the reason for the degradation in hardness in the 9Cr alloy with further homogenization, a cooling rate experiment was performed on the 9Cr extruded bar to determine if a martensite transformation was operating and had any effect on properties. Three specimens were aged at 1100°C for 5 min and then cooled either by quenching in water, cooling in air or cooling in the furnace to 700°C (cooling took 1.7 h) and holding for two hours. Resulting hardness measurements are given in Table 4. From comparison of Tables 3 and 4, it can be shown that the hardness of the 9Cr alloy can be raised by suitable heat treatment procedures, but the hardness can also be reduced to values on the order of 20 R_C by furnace cooling. This suggests that the yttria is reacting with the carbon and being redistributed so that hardness is controlled by the martensite structure. Therefore, mechanical alloying benefits are probably not retained.

Table 4. Hardness as a function of cooling rate for the 9Cr alloy

Condition	Hardness (R _C)
Water quenched	44.5
Air cooled	42.2
Furnace cooled to 700/2h	19.2

Although the fabrication of extrusions from the experimental mechanical alloys turned out quite well, there are several areas which could benefit from some additional work. One area is the effect of a smaller batch size and extended milling times on the degree of mechanical alloying and the need for homogenization. The batch size used in this program corresponded to a 15:1 ball-to-charge ratio. The INCO patents on commercial alloys MA956 and MA957² refer to a 20:1 ball-to-charge ratio. The higher ratio would unfortunately mean that more batches would be required to process the same amount of powder. Another area in need of further study is the outgassing procedure used to evacuate the powder cans before HIPing. There is no reliable way of predicting, from theory, the temperatures at which various gas species will evolve during outgassing. We have found that residual gas analysis (RGA) is an effective technique for detecting small amounts of gas evolved during a vacuum heat treatment. This information can be used to establish an effective outgassing schedule ultimately leading to reduced porosity in the consolidated product. The additional work described should result in a major improvement in the homogeneity and quality of mechanically alloyed Fe-Cr extrusions.

CONCLUSIONS

Two low activation ferritic ODS alloys have been successfully manufactured using mechanical alloying processes and extruded into bar. One of the alloys, Fe-14Cr-1.0Ti-0.5W-0.25Y₂O₃, is considered worthy of further study as a candidate first wall material.

FUTURE WORK

Fabrication of two more, ODS alloys is planned for the next reporting period.

REFERENCES

1. D. J. Sherwood, A. L. Ward, and G. D. Johnson, Nuc. Tech. 78, 83 (1987).
2. Cairns et al., U.S. Patents 3,837,930 (September 24, 1974) and 3,992,161 (November 16, 1976).

Figure Captions

- Figure 1. The 14Cr and 9Cr mechanically alloyed powder samples were mounted in molding compound, polished and etched (Vilella's reagent) to reveal a cross section of the particles. The 14Cr alloy is shown in (a) and the 9Cr alloy in (b).
- Figure 2. Polished and etched (Vilella's reagent) sections of HIPed 14Cr and 9Cr coupons are shown in (a) and (b). ReHIPed 14Cr and 9Cr are shown in (c) and (d). The most notable features are apparent remnant precursor particles.
- Figure 3. Lower magnification photomicrographs of 9Cr HIPed coupon in (a) and reHIPed and homogenized 9Cr in (b) show typical distribution of remnant precursor powder particles.
- Figure 4. Microstructure of extrusions before homogenization (a) and (b) and after homogenization (c) and (d). The most obvious change after homogenization is the increase in pore size.
- Figure 5. As-extruded bars MTU #1 (a) and MTU #2 (b) showing both sides of each bar at low magnification. Sufficient uncracked material was available for tube fabrication studies.

(a)

(b)

Figure 1. The 14Cr and 9Cr mechanically alloyed powder samples were mounted in molding compound, polished and etched (Vilella's reagent) to reveal a cross section of the particles. The 14Cr alloy is shown in (a) and the 9Cr alloy in (b).

(a)

(b)

(c)

(d)

Figure 2. Polished and etched (Vilella's reagent) sections of HIPed 14Cr and 90Cr. The images are shown in (a) and (b). HIPed 14Cr and 90Cr are shown in (c) and (d). The scale bar indicates 100μm.

(a)

(b)

Figure 3. Lower magnification photomicrographs of 9Cr HIPed coupon in (a) and reHIPed and homogenized 9Cr in (b) show typical distribution of remnant precursor powder particles.

(a)

(c)

Figure 4. Microstructure
after homoge
homogenizati

Figure 5. As-extruded bars MTU #1 (a) and MTU #2 (b) showing both sides of each bar at low magnification. Sufficient uncracked material was available for tube fabrication studies.

END

DATE FILMED

01 / 08 / 91