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Faulkner et al.

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[54] **COMPOSITE METAL PRODUCTS**

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[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **B32b 15/00**
[58] **Field of Search**.............................29/194, 196.6

[56] **References Cited**

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[57] **ABSTRACT**

A composite product comprising a foundation alloy containing Ni to 45%, Cr 15 to 25%, C up to 0.1%, titanium and/or niobium in a total of about from 1 to 4%, Al 0 to 4%, Mo 0 to 10%, balance Fe, clad with an alloy containing Cr 45 to 60%, C up to 0.04%, Zr 0.1 to 4%, balance Ni. An intermediate layer of nickel can be included between the foundation and the cladding.

5 Claims, No Drawings

COMPOSITE METAL PRODUCTS

The present invention relates to composite metal products and, more particularly, composite products comprising a high strength foundation alloy clad with a corrosion-resistant alloy (or cladding alloy), which alloys are metallurgically bonded.

In heat-exchanger applications such as those in power stations and the like, it is desirable that the tubes in the super-heater possess both good high temperature strength and good corrosion resistance to super-heated steam and hot flue gases. Where, in such applications, two dissimilar alloys are in metallurgically bonded contact, as in the case of such composites at high temperatures, e.g., greater than 600°C., for long periods of time, interdiffusion of the major elements across the interface between the respective alloys can occur. Although a limited degree of diffusion is necessary for the formation of good bonds at the interface of the foundation and cladding members, if the interdiffusion zone in either member exceeds about 5 to 30 μm, the respective alloy compositions of the two component members may be changed, thereby changing their respective properties and/or there may be an undesirable accumulation or depletion of certain elements in the region of the interface which may cause embrittlement and failure.

We have now surprisingly found that the degree of interdiffusion in certain composite products of the above general type can be reduced by carefully controlling the composition of the foundation alloy and adding zirconium to the cladding alloy.

An object of the present invention is to provide a composite product exhibiting good high temperature strength and corrosion resistance and exhibiting minimal interdiffusion.

According to the invention a composite product comprises a foundation member of an alloy containing, by weight, from about 10 to about 45 percent nickel; from about 15 to about 25 percent chromium; less than about 0.01 percent free carbon (i.e., carbon that is not present as titanium, niobium or chromium carbide) with the total amount of carbon not more than about 0.1 percent, preferably at least about 0.01 percent, e.g., 0.04 to 0.07 percent carbon; titanium and/or niobium in a total amount of from about 1 to about 4 percent, preferably from 1 to 3 percent; up to about 4 percent aluminum; up to about 10 percent molybdenum; and the balance, except for impurities, being iron; clad with (i.e., metallurgically bonded to) an alloy containing, by weight, from about 45 to about 60 percent chromium; up to about 0.04 percent carbon; and from about 0.1 to about 4 percent, preferably from 0.5 to 2 percent zirconium; and the balance, except for impurities, being nickel.

Generally speaking in the composite products of the invention, interdiffusion of major elements will be limited to within the acceptable distance of 5 to 30 μm from the interface between the alloys after exposure at temperatures up to about 700°C. for times of up to 1,000 hours.

The zirconium addition in the cladding alloy will generally only inhibit major element diffusion across the interface when the amount of free carbon in the foundation alloy is low, i.e., below 0.01 percent. If there is a relatively large amount of free carbon in the foundation alloy, then this element will tend to diffuse across the interface between the foundation and the cladding, into the cladding, thereby deleteriously affecting the efficacy of the zirconium in mitigating diffusion of major elements by tying up free zirconium. However, a minimum carbon content of about 0.01 percent is preferred in the foundation alloy to provide sufficient strength at high temperatures. Similarly, carbon in the cladding alloy should be avoided and the carbon content thereof must not exceed 0.04 percent. The total carbon content of the foundation alloy preferably does not exceed 0.07 percent and in addition a strong carbide forming element such as titanium or niobium or both, must be present therein in a total amount of about from 1 percent to 4 percent. Other strong carbide forming elements which may be used are tantalum and vanadium.

The nickel content of the foundation alloy should be at least 10 percent to ensure adequate strength. However, when the nickel content exceeds 45 percent, chromium carbides tend to form in preference to titanium or niobium carbides. This is because the titanium and niobium form Ni_3Ti and Ni_3Nb, respectively. Chromium carbides are not as stable as either titanium carbide or niobium carbide and are therefore less effective in combining with the free carbon in the alloys.

The chromium content of the foundation alloy must be at least 15 percent to ensure adequate corrosion resistance. However, amounts of chromium above 25 percent could lead to embrittlement by the formation of sigma phase.

Aluminum strengthens the foundation alloys and up to 4 percent thereof may be present for this purpose. Preferably the aluminum content is between about 1 and 4 percent. Molybdenum may be added as a solid solution strengthener and as an additional carbide forming element. Amounts up to 10 percent molybdenum may be employed although, preferably, the molybdenum content does not exceed 3 percent. Some examples of various alloy compositions that may be utilized as the foundation member of the present invention are given in Table I.

TABLE I

Alloy	C	Mn	Si	Cr	Ni	Cu	Mo	Fe	Ti	Al	B	S	Nb
1	.05	1.35	.50	15.0	26.0		1.3	Bal.	2.0	0.2	.015		
2	0.05	0.75	0.50	20.5	32.0	0.25		44.5	1.13			0.008	
3	0.07			16.5	43.5		3.3	Bal.	1.2	1.2			
4	0.05	5.8		15.8	10.3		1.08	Bal.					1.2

The cladding alloys possess good corrosion resistance and good compatibility with the foundation alloys in that they form strong bonds with the foundation alloy. Some examples of various cladding alloy compositions useable in the present invention are given in Table II.

TABLE II

Alloy	Ni	Cr	C	N	Zr

11	Bal.	49.5	.011	.022	1.15
12	Bal.	49.5	.021	.070	1.85
13	Bal.	60.0	.021	.068	1.15
14	Bal.	60.0	.006	.060	1.80
15	Bal.	60.0	.005	.110	1.70
16	Bal.	60.0	.021	.063	1.15

The composite products of the invention may be readily produced by techniques such as hot-rolling, co-drawing and co-extrusion, including co-extrusion of a powder-metallurgically produced sintered cladding element with a preformed foundation element to provide a metallurgical bond between the alloy elements forming the composite. For example, co-extrusion can be conducted by disposing the body intended for the foundation within the body (e.g., a tube) intended for the cladding and carrying out the co-extrusion process at about 1,100° to 1,150°C. In such drawing and extrusion processes it is, of course, necessary that the cladding alloy should be adequately workable and to ensure this, the amount of zirconium present therein preferably is at least about 0.5 percent and the nitrogen content thereof should be low, preferably not more than 0.1 percent. Among the various forms in which the composite article of the present invention can be made are sheet, strip, tubing, bar, and rod, for example.

EXAMPLE

The composite articles shown in Table III were made by co-extruding bar forms.

TABLE III

Article number	Foundation alloy composition (percent) C	Cr	Mo	Ti	Al	Mn	Ni	Fe	Nb	Cladding alloy composition (percent) C	Cr	Zr	Ni
1	0.07	16.5	3.3	1.2	1.2		43.5	Balance		0.018	49	0.85	Balance.
A	0.07	16.5	3.3	1.2	1.2		43.5	do		0.018	49		Do.
2	0.05	15.8	1.08			5.8	10.3	do	1.2	0.018	49	0.85	Do.
B	0.05	15.8	1.08			5.8	10.3	do	1.2	0.018	49		Do.
C	0.047	20.0		0.4	0.4		31.0	do		0.018	49	0.85	Do.
D	0.047	20.0		0.4	0.4		31.0	do		0.018	49		Do.

Articles No. 1 and 2 of Table III are in accordance with the invention, while Articles A to D are outside the invention and are included for reference purposes. The composite articles were sectioned and heated at 700°C. for either 1,000 or 10,000 hours. After polishing, the carbide structures at the interfaces were electrolytically etched in either 10N potassium hydroxide solution or hydrogen fluoride solution or chemically etched in 2 percent nital. The samples were then examined optically and the diffusion distances of the major elements across the interface between the foundation and the cladding members, i.e., the depths of enrichment by said elements, were measured with an electron microprobe analyzer, the results being set forth in Table IV.

TABLE IV

Article No.	Element Studied	Time at 700°C. (hrs.)	Diffusion Distance (μm)
1	Fe.	1,000	20
1	Fe.	10,000	45
A	Fe.	1,000	50
A	Fe.	10,000	75
2	Fe.	1,000	25
B	Fe.	1,000	55
2	Ni.	1,000	5
B	Ni.	1,000	15
2	Cr.	1,000	5
B	Cr.	1,000	15
C	Fe.	1,000	55
D	Fe.	1,000	55

It can be seen from the results given in Table IV that in the articles designated Nos. 1 and 2 interdiffusion of iron has been limited to acceptable proportions, in

marked contrast to the experience with the articles designated A, B, C, and D. In addition, in Articles 2 and B, although the problem of interdiffusion of nickel and chromium was not severe, the effect of the presence of zirconium in further reducing interdiffusion can be clearly seen.

A further benefit in the form of further reduced interdiffusion can be derived by interposing an interlayer consisting essentially of nickel between the foundation and cladding members. This interlayer acts as a sink for iron and chromium that might diffuse out of the cladding and foundation members, while diffusion of nickel from the interlayer into the cladding and foundation members is not found to be deleterious to the properties of the composite product. Advantageously the interlayer is from 10 to 40 μm thick, e.g., 25 μm, but it may be greater if the composite article is to be exposed for long periods or to particularly high temperatures.

The composite product may be produced by working an assembly of the foundation and cladding alloys with an intermediate layer of nickel. The nickel layer may be provided by known methods (e.g., plating) on the foundation element or on the cladding element before producing the composite product, or a nickel body (e.g., sheet) may be interposed between the foundation and the cladding elements before producing the composite product. The thickness of the nickel layer initially should be such that the desired thickness of nickel remains after the working is completed.

Whether or not a nickel interlayer is employed, the foundation alloy preferably has a total carbon content of at least 0.01 percent in order that it may have good strength at high temperatures.

The composite products of the invention are particularly suitable for use in heat-exchanger applications but may be employed in other applications demanding high strength and good corrosion resistance at elevated temperatures.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A composite metal product comprising a foundation member and a cladding member metallurgically bonded together, said foundation member being made of an alloy consisting essentially of by weight, about 10 percent to about 45 percent nickel, about 15 percent to about 25 percent chromium, about 1 percent to about 4 percent of an element from the group consisting of titanium and niobium, up to about 4 percent aluminum, up to about 10 percent molybdenum, carbon up to about 0.1 percent, and the balance iron, and said cladding member being made of an alloy consisting es-

sentially of about 45 percent to about 60 percent chromium, less than about 0.04 percent carbon, about 0.1 percent to about 4 percent zirconium, and the balance nickel.

2. A composite metal product as defined in claim 1, wherein the carbon content of said foundation member is about 0.04 percent to about 0.07 percent.

3. A composite metal product as defined in claim 1, wherein the carbon content of said foundation member is at least about 0.01 percent.

4. A composite metal product as defined in claim 1, where said foundation alloy contains not more than 3 percent of titanium and/or niobium.

5. A composite metal product as defined in claim 1, wherein said cladding member contains about 0.5 percent to about 2 percent zirconium.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,718,443 Dated September 13, 1974

Inventor(s) Roy Gwyn Faulkner et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Abstract, line 2, "Ni to 45%" should read -- Ni 10 to 45% --; line 10, "to" should read -- 10% --.

Signed and sealed this 26th day of November 1974.

(SEAL)
Attest:

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Attesting Officer

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Commissioner of Patents