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As-cast microstructure, room temperature hardness and high temperature creep deformation of an equimolar quaternary CoNiFeCr alloy and of two slightly modified versions

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Abstract: The equimolar CoNiFeCr composition can be considered as a Mn-free Cantor alloy. Removing manganese allowed improving significantly its hot oxidation resistance in air, even for temperatures up to 1100°C. Another beneficial consequence of Mn suppression is potentially a much better creep-resistance, which is also expected to increase with addition of Ti and Ta. This is what was explored in this work. After microstructure and hardness control by electron microscopy and Vickers indentation (load: 1kg), flexural creep tests were carried out at 1100°C for a centered 3 points bending solicitation under constant load inducing locally 10 MPa as maximal tensile stress. The CoNiFeCr alloy and its version containing Ti are single-phased while a second phase rich in tantalum is present in the Ta-containing one. Concerning the creep behavior, the CoNiFeCr alloy deformed much slower than the Cantor alloys. The versions alloyed with Ti and Ta resisted creep better than the former alloy. The Ta-containing CoNiFeCr alloy demonstrated the best resistance, with a particularly slow deformation.

Keywords: MPEA; Titanium; Tantalum; Hardness; Creep behavior

1. Introduction

High entropy alloys, a new family of metallic alloys emerged in the earliest 2000's [1], have now taken a broad place. One of their most representative member is the equimolar CoNiFeMnCr alloy (Cantor's alloy) [2]. The latter one is still of interest, as demonstrated by numerous recent studies concerning it or its not equimolar derivatives (e.g. [3–7]). These alloys offer many interesting properties at not too high temperatures down to very low temperatures. In contrast, their behaviors at elevated temperatures do not allow these alloys being potential substitutes superalloys, alloys rich in nickel and/or cobalt [8,9], elements expensive and with possible problem of availability [10,11]. This is seemingly manganese which is responsible of the inability of such alloys to be used at 1000°C and beyond, since the presence of Mn in significant quantity is deleterious to bad creep resistance [12] as well as to hot oxidation resistance [13]. To try keeping alloys derived from the Cantor composition, high temperature properties improvements were searched by decreasing the Mn content (and increasing the Cr one) with some success. Higher creep resistance and oxidation resistance were effectively observed [14,15]. The purpose of the present work is to go beyond these latter alloys by entirely removing Mn from the composition. Since the obtained quaternary alloy cannot be longer a real high entropy alloy with the benefices brought by the HEA principle, two other elements – Ti and Ta – were added to promoting increased mechanical properties to the so obtained quinary alloys.

2. Experimental

An equimolar CoNiFeCr alloy, the same with titanium added in quantity allowing reaching 2 wt.% Ti, and a third one resulting from the addition of tantalum to reach 6 wt.%Ta were prepared from pure elements (>99.9%) and obtained as small ingots (mass: 40g, shape: ovoid, dimension: equivalent diameter ≈2 cm) by high frequency induction melting under inert atmosphere. Cutting with a precision metallographic saw led to parts for control of both chemical composition and microstructures, macro-indentation, and creep tests. For chemical and metallographic control, the parts were embedded in a mixture involving resin and hardener, ground with SiC papers (#240 to #1200 grit), water washed and ultrasonically cleaned, and polishing with a textile disk regularly enriched with spray of 1 µm alumina hard particles.

The obtained mirror-like samples were introduced in a scanning electrons microscope (SEM: JEOL JSM 6010 LA) equipped with an Energy Dispersion Spectrometry (EDS) device. Microstructure examination was carried out in back scattered electrons (BSE) imaging. Chemical composition was assessed with five full frame analyses.

Hardness of the alloys was performed according to the Vickers procedure. The applied load was 1 kg and ten indentations were realized.

12 mm – long parallelepipeds with {1 to 1.5 mm} × {1.5 to 2 mm} rectangular sections were prepared for performing the creep tests (surface states: ground with #1200 SiC papers). Each parallelepiped was introduced in the hot zone of a thermo-dilatometer from SETARAM, modified and adapted to allow centered three points bending test. The load was applied – progressively – to reach the value calculated to induce a 10 MPa tensile stress in the middle of the bottom face of the parallelepiped. This load, of several hundreds grams, was calculated taking into account the exact transversal dimensions of each parallelepiped sample. After closing a continuous gas sweep (pure Ar) was generated for the protection of the sample during the high temperature exposure. The flexural creep test was performed at the 1100°C constant temperature, for a maximal duration of 200 hours (to guarantee the availability for other tests).

3. Results and discussion

3.1 Control of the chemical compositions and of the microstructures of the three alloys

According to the results of a five full frame EDS analyses, the obtained contents in Co, Ni, Fe, Cr and Ta well correspond to the targeted ones. This is not the same for titanium, the high reactivity of which led to significant “loss of ignition” during melting. This is due to the oxygen and nitrogen traces present in the “pure” argon atmosphere surrounding the liquid alloy in the fusion chamber. Only 1.5 wt.%Ti were thus obtained in the CoNiFeCrTi alloy, against the wished 2 wt.%.

The microstructures of the three alloys are illustrated by the SEM/BSE micrographs presented in Figure 1. The CoNiFeCr and CoNiFeCrTi alloys are single-phased (FCC solid solution), while the CoNiFeCrTa alloy is composed of two distinct phases: a principal phase made of a FCC solid solution of Co, Ni, Fe, Cr and about 1 wt.%Ta, and another phase, very rich in tantalum, present in the interdendritic spaces. The principal phase (matrix) of the Ta – containing alloy is not chemically homogeneous since the periphery of dendrites, brighter than the core, are enriched in tantalum. Solidification was obviously accompanied by release of tantalum in the neighbor liquid (segregation).

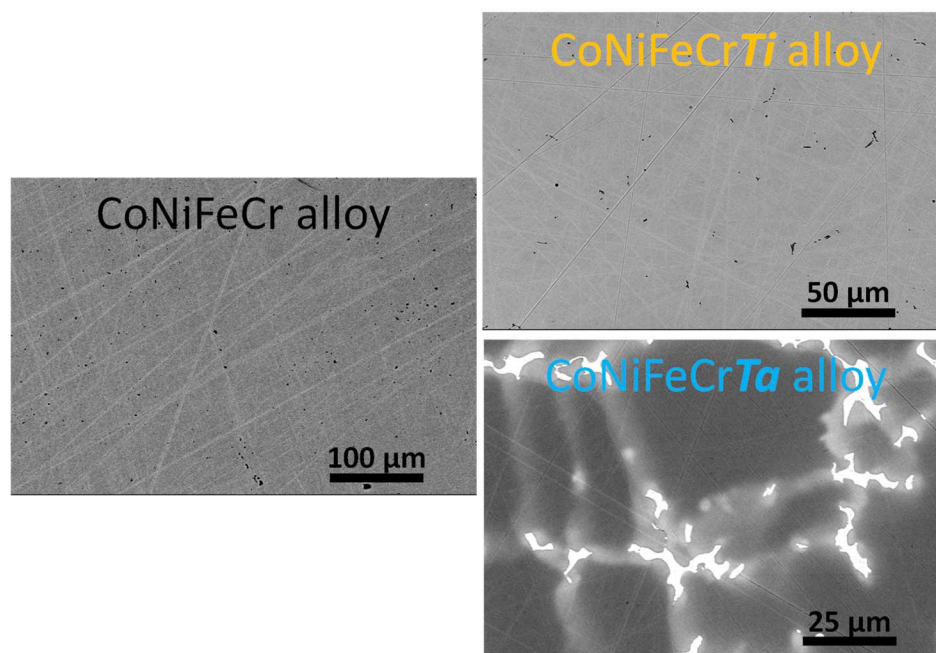
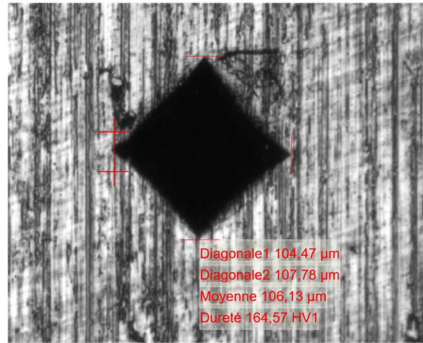


Figure 1. SEM/BSE micrographs illustrating the microstructures of the three alloys in their as-cast condition

3.2 Vickers macro-indentation results

Ten indentations under a 1 kg load were performed on the three alloys (Figure 2). The CoNiFeCr alloy presents a hardness of about 140 Hv_{1kg}. This value is comprised between the 100 Hv of {Ni or Fe}–30 wt.%Cr alloys and the 300 Hv of the Co–30 wt.%Cr one [16–18], which appears as logical. This not high level let think that this alloy can be easily machined, as reported in many studies. Ta and Ti additions obviously induce an increase in hardness: about 165 Hv for The CoNiFeCrTi alloy and about 175 Hv for the CoNiFeCrTa one. Taking into account the [Min, MAX] ranges defined by the ten measured hardness values the hardening by addition of Ti or Ta is significant and suggests that other mechanical properties (e.g. tensile resistance at all temperatures and creep resistance) may be improved. 6 wt.%Ta seems more efficient than 2 (1.5 in fact) wt.%Ti for increasing hardness but this is just a tendency since the difference between the two is not significant (overlapping of the two [Min, MAX] ranges).



From 10 Vickers indentations (load = 1kg):

	Min	MAX	<u>average</u>
CoNiFeCr	136.4	147.3	142.1
CoNiFeCrTi	160.4	172.2	165.7
CoNiFeCrTa	165.0	181.1	174.4

Figure 2. Hardness of the three alloys (Vickers, load: 1 kg)

3.3 Creep tests results

The principle of the mechanical solicitation (three points centered bending test) is reminded by a scheme given in Figure 3 (right) and the extremity of the alumina apparatus where the parallelepiped sample is placed is photographed in the same figure (left). The {1100°C, 10 MPa} test of the CoNiFeCr alloy was stopped before reaching the 200 hours since it deformed rather quickly. In contrast, the deformation kinetics of the two other alloys were much slower and the initially scheduled 200 hours durations were respected.

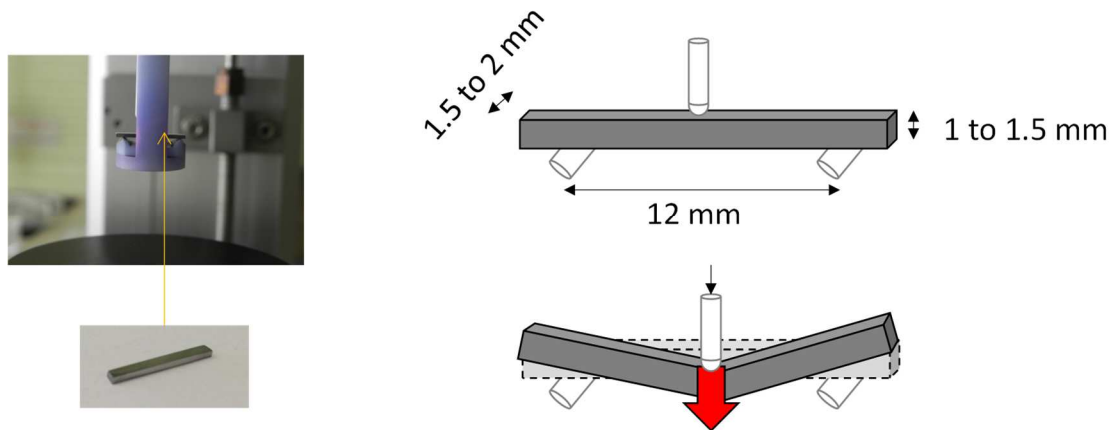


Figure 3. Principle of the three points flexural creep tests; photographs of the extremity of the alumina apparatus and of a parallelepiped sample before test (left) ; scheme (right)

At the end of the tests and after complete cooling, the apparatus was opened at laboratory temperature and the crept samples were exited. Figure 4 show illustrates their appearance: more (CoNiFeCr) or less (CoNiFeCrTi and CoNiFeCrTa) deformed, and oxidized despite the circulation of pure argon. Due to the constant renewal of “pure” argon (thus renewal of oxygen present as traces in this gas), oxidation occurred and its progress was maintained during the 200 hours, this resulting in significant oxidation visible at the end of experiment (however oxidation not so developed as if test was performed in air).

The three obtained deformation curves are plotted together in Figure 5, where the deformation curves obtained earlier in the same conditions (same apparatus, temperature and stress) for two other alloys are added for comparison. These two reference alloys are an original Cantor alloy (equimolar CoNiFeMnCr) and a Cantor alloy added with carbon and tantalum to develop an interdendritic network of TaC carbides. Both were elaborated with the same melting apparatus and following the same procedure as the three alloys of this study.

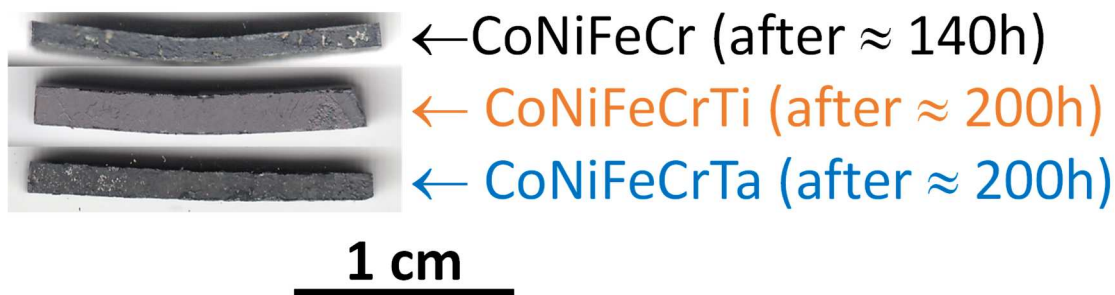


Figure 4. Photographs of the three samples at the end of creep test

One can see that, at the beginning, the CoNiFeCr alloy deformed as fast as the reference Cantor's alloy but only during the first 50 hours. Thereafter its deformation decelerated significantly (secondary creep regime also called steady state?) while, for the Cantor's alloy, the central part of the sample came into contact with the alumina base after about 100 hours. The two other alloys of this study deformed much slower than the CoNiFeCr alloy. The central deformation of the CoNiFeCrTi alloy was only a little more than 300 μm after 200 hours and its deformation rate still went on slightly decelerating. It behaved even a little better than the TaC-reinforced Cantor alloy (the second reference alloy). This is the CoNiFeCrTa alloy which is the most resistant with only about 100 μm of deformation after 200 hours.

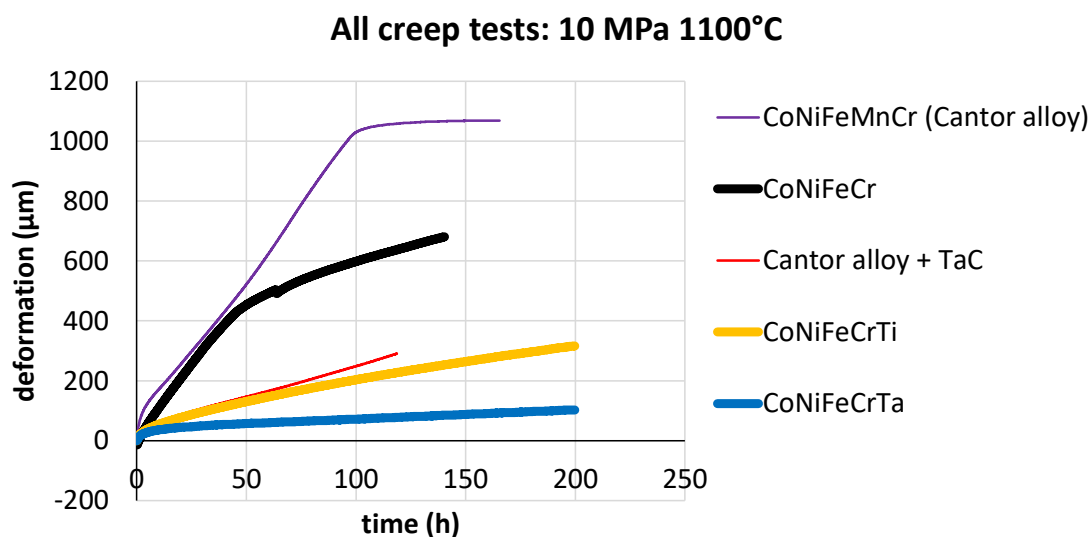


Figure 5. The three obtained curves (thickest lines); comparison with the Cantor alloy and its TaC-added version (thinner lines)

By plotting the deformation rate with time and using a regression straight line for the obviously stabilized kinetic part of and by exploiting its equation one can determinate the deformation rate during the steady state creep. This gives 2 $\mu m h^{-1}$ for the CoNiFeCr alloy (Figure 6), 1 $\mu m h^{-1}$ for the CoNiFeCrTi alloy (Figure 7) and 0.4 $\mu m h^{-1}$ for the CoNiFeCrTa alloy (Figure 8). Even if 1100°C is not a very high temperature and 10 MPa is a rather low stress, these deformations are remarkably slow. One must note that the order of these deformation rates is the same as the order of the average hardness measured above.

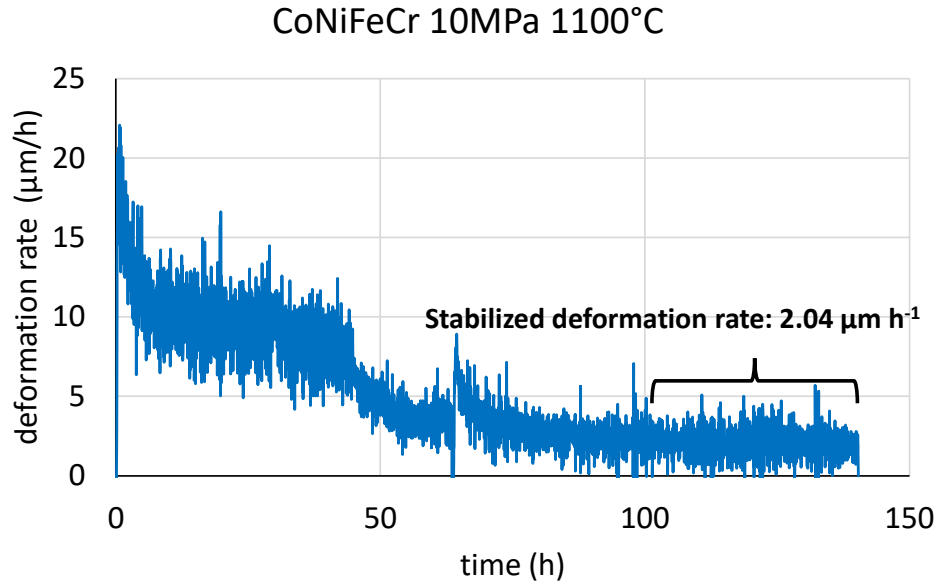


Figure 6. Evolution with time of the deformation rate of the CoNiFeCr sample; visualization on the stabilized rate part and determination of the corresponding stabilized deformation rate

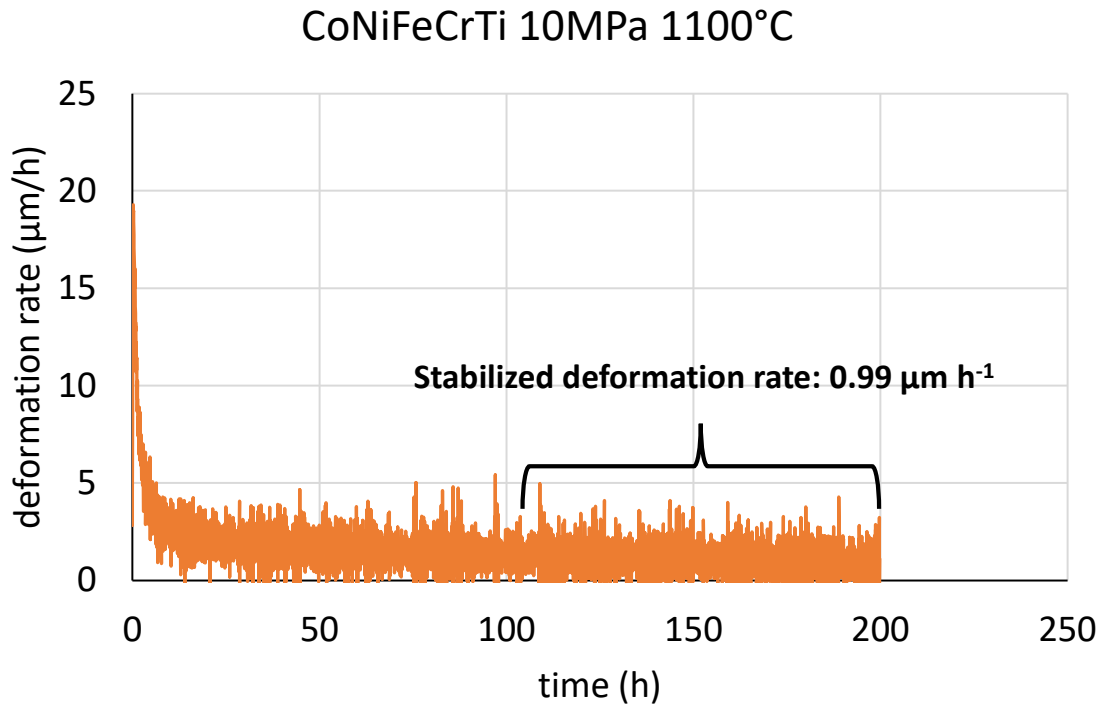


Figure 7. Evolution with time of the deformation rate of the CoNiFeCr sample; visualization on the stabilized rate part and determination of the corresponding stabilized deformation rate

4. Conclusion

By removing all manganese from the Cantor alloy a first improvement was obtained for the creep behavior at 1100°C. More significant progress in creep resistance occurred when titanium or tantalum was added. The

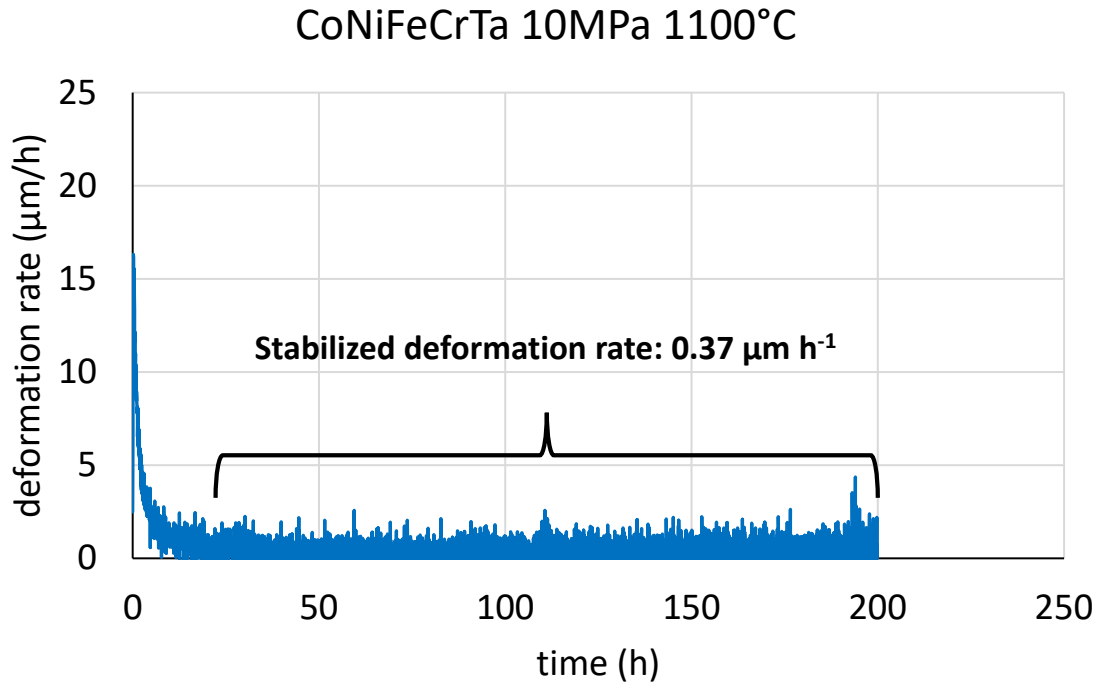


Figure 8. Evolution with time of the deformation rate of the CoNiFeCr sample; visualization on the stabilized rate part and determination of the corresponding stabilized deformation rate

obtained alloys are both more resistant than the Cantor alloy strengthened by a rather dense network of TaC carbides which may cause problem of machinability. With these two solid solution strengthened Cantor-inspired alloys high mechanical performance at high temperature seems having been reached, with preserved hardness and machinability. Now new alloys can be imagined to reinforce more the CoNiFeCrTi alloy by introducing more Ti in the composition, and to decrease the cost of the CoNiFeCrTa which is perhaps too rich in tantalum (presence of Ta-rich phase not necessarily useful, phase remaining to be identified).

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